

# Estuarine and Coastal Ocean Carbon Paradox: CO<sub>2</sub> Sinks or Sites of Terrestrial Carbon Incineration?

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Annu. Rev. Mar. Sci. 2011. 3:123–45

First published online as a Review in Advance on October 18, 2010

The *Annual Review of Marine Science* is online at [marine.annualreviews.org](http://marine.annualreviews.org)

This article's doi:  
10.1146/annurev-marine-120709-142723

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1941-1405/11/0115-0123\$20.00

## Keywords

air-sea CO<sub>2</sub> exchange, carbon flux, dissolved inorganic carbon dynamics, estuary, salt marsh, continental shelf

## Abstract

Estuaries are a major boundary in the land-ocean interaction zone where organic carbon (OC) and nutrients are being processed, resulting in a high water-to-air carbon dioxide (CO<sub>2</sub>) flux (~0.25 Pg C y<sup>-1</sup>). The continental shelves, however, take up CO<sub>2</sub> (~0.25 Pg C y<sup>-1</sup>) from the atmosphere, accounting for approximately 17% of open ocean CO<sub>2</sub> uptake (1.5 Pg C y<sup>-1</sup>). It is demonstrated here that CO<sub>2</sub> release in estuaries is largely supported by microbial decomposition of highly productive intertidal marsh biomass. It appears that riverine OC, however, would bypass the estuarine zone, because of short river-transit times, and contribute to carbon cycling in the ocean margins and interiors. Low-latitude ocean margins release CO<sub>2</sub> because they receive two-thirds of the terrestrial OC. Because of recent CO<sub>2</sub> increase in the atmosphere, CO<sub>2</sub> releases from low latitudes have become weaker and CO<sub>2</sub> uptake by mid- and high-latitude shelves has become stronger, thus leading to more dissolved inorganic carbon export to the ocean.

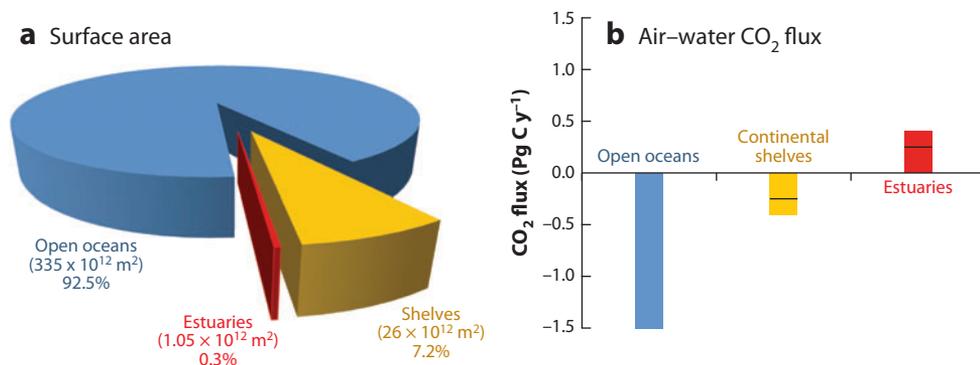
**Estuary:** a semi-enclosed coastal body of water between the river mouth and tidewater, where freshwater mixes with seawater

**Continental shelf:** area from shoreline to the shelf break, usually at 100- to 200-m depths

## 1. INTRODUCTION

Where, when, and how organic carbon (OC) is decomposed into carbon dioxide (CO<sub>2</sub>) and lost to the atmosphere through the coastal continuum of rivers, estuaries, marshes, and continental shelves before reaching the slope and the open ocean is still controversial. Several recent articles that reported global estuarine and coastal ocean CO<sub>2</sub> fluxes concluded that although the global estuarine area is very small, its CO<sub>2</sub> degassing flux is as large as the CO<sub>2</sub> uptake by the continental shelf, and that both flux terms are significant in the global CO<sub>2</sub> flux (**Figure 1**) (Borges 2005, Borges et al. 2005, Cai et al. 2006, Chen & Borges 2009). Excellent reviews have also been presented from global and historical perspectives explaining the control mechanisms on coastal CO<sub>2</sub> fluxes (Smith & Hollibaugh 1993, Wollast 1998, Ducklow & McCallister 2004, Mackenzie et al. 2004). I will follow this tradition and organize information derived from a few individual systems in a global and historical context to illustrate the control mechanisms of coastal CO<sub>2</sub> fluxes.

In this review article, I examine CO<sub>2</sub> fluxes across several boundaries at the land-ocean interface, with a focus on the estuary-marsh interaction, to see what can be learned and what is missing in our current research and thinking. This review is not intended to be inclusive of all known systems in coastal waters. Further, biogeochemical processes that alter larger river fluxes in their plume zones will not be discussed, as their impact often extends to the outer shelf and the open ocean and the topic deserves separate treatment. On the sea side, I will not discuss the shelf-open ocean exchange, which is very important but poorly understood. In addition, terrestrial material fluxes are treated as boundary conditions and are taken from existing review articles. Although the importance of coastal CO<sub>2</sub> fluxes is emphasized throughout this review, I do not intend to provide another global carbon flux and budget analysis, as this has been attempted by many in the past



**Figure 1**

Surface areas of estuaries, continental shelves, and open oceans (*a*) and their estimated air-water CO<sub>2</sub> fluxes (*b*). Open ocean CO<sub>2</sub> flux (*blue*) is from Takahashi et al. (2009); continental shelves (*yellow*) and estuarine (*red*) fluxes are from Borges et al. (2005) and Cai et al. (2006). The most likely flux for shelves ( $-0.25 \text{ Pg C m}^{-2} \text{ y}^{-1}$ ) and estuaries ( $+0.25 \text{ Pg C m}^{-2} \text{ y}^{-1}$ ) suggested by myself is marked with a black bar. Woodwell et al. (1973) estimated a global estuarine open-water area of  $1.36 \times 10^{12} \text{ m}^2$  and an intertidal salt marsh area of  $0.38 \times 10^{12} \text{ m}^2$  (i.e., the total area is  $1.74 \times 10^{12} \text{ m}^2$ ). These values include large bays (the Chesapeake Bay and St. Lawrence Gulf) and inland seas (i.e., the Baltic Sea). The Baltic Sea is removed from the estuarine area here as it is listed as continental shelf in all the shelf CO<sub>2</sub> syntheses. Then the global open estuarine water area (including both river-dominated and nonriverine coastal lagoons) is  $1.05 \times 10^{12} \text{ m}^2$ . The coastal ocean (continental shelf) area is from Walsh (1988). Other global area information used in this review for global flux calculations includes total salt marshes and mangroves:  $0.38 \times 10^{12} \text{ m}^2$  (Woodwell et al. 1973); mangrove:  $0.18 \times 10^{12} \text{ m}^2$  (Duarte et al. 2005; Bouillon et al. 2008); and marsh:  $0.20 \times 10^{12} \text{ m}^2$  by the difference.

(see above references and most recently, Liu et al. 2010). Rather, I will focus on explaining how two types of terrestrial carbon fluxes, riverine versus marsh-derived, would affect CO<sub>2</sub> release/uptake in coastal waters. Modeling various physical and biogeochemical processes that are critical to CO<sub>2</sub> fluxes in coastal oceans is reviewed by Hofmann et al. (2011) in this volume.

Early on, Walsh et al. (1981) proposed that “biological export of shelf carbon is a neglected sink of the global CO<sub>2</sub> cycle.” They envisioned that riverine anthropogenic inputs could provide the nutrients needed for the extra CO<sub>2</sub> uptake. Subsequent fieldwork at the U.S. Middle Atlantic Bight suggested that particulate organic carbon (POC) export was rather small (Rowe et al. 1988), although dissolved organic carbon (DOC) export (Vlahos et al. 2002) and CO<sub>2</sub> uptake were observed (DeGrandpre et al. 2002).

Another school of thought, however, has argued and gained great acceptance that the ocean, and in particular, the coastal ocean, must be net heterotrophic and, during steady-state or preindustrial conditions, also a CO<sub>2</sub> source because riverine OC is largely respired there (Smith & Mackenzie 1987, Smith & Hollibaugh 1993). Such CO<sub>2</sub> evasion has been observed widely in estuaries and nearshore systems (Frankignoulle et al. 1996, Cai & Wang 1998, Gattuso et al. 1998, Cai et al. 2003b) but rarely in major continental shelves.

Whereas a synthesis of terrestrial C and N flux to, and their fate in, the ocean (Section 2) strongly suggests that the coastal ocean must be heterotrophic (i.e., burning OC and releasing CO<sub>2</sub>), current syntheses of air-sea CO<sub>2</sub> flux in coastal oceans (Section 5) have shown that most shelves are CO<sub>2</sub> sinks, except those in the low latitudes. It is also puzzling that the large CO<sub>2</sub> degassing flux in estuaries (**Figure 1**) seems to suggest that most terrestrial OC export must be decomposed there. Throughout this review, I will show that the large amount of CO<sub>2</sub> degassing observed in coastal waters must be supported by lateral transport of carbon from the surrounding coastal wetlands, which are highly productive. Riverine OC, however, is likely bypassing estuaries and being delivered directly to the coastal oceans, mostly to the low latitudes, for respiration there. Furthermore, increased *p*CO<sub>2</sub> in the atmosphere must have changed the driving force for air-sea CO<sub>2</sub> exchange in seasonally heterotrophic shelf areas, which might have been a CO<sub>2</sub> source in the preindustrial age, to a CO<sub>2</sub> sink (or a reduced source) today. Therefore, increased *p*CO<sub>2</sub> in the atmosphere, increased inorganic nutrient flux, and decreased sedimentary OC supply to the coastal ocean (due to damming) likely will lead to further uptake of atmospheric CO<sub>2</sub> in the coastal zone.

## 2. TERRESTRIAL FLUXES OF CARBON, NITROGEN, AND PHOSPHORUS

### 2.1. Heterotrophic versus Autotrophic Loading

The terrestrial biosphere is autotrophic; i.e., it synthesizes more OC than it respire (Schlesinger 1997). The OC export from the land to the ocean subsidizes a net heterotrophic process in the ocean as a whole and, historically, with the ocean returning CO<sub>2</sub> to the atmosphere (Mackenzie et al. 2004, Sarmiento & Gruber 2006). Human activities on land in past centuries have increased sediment runoff and the associated POC flux to the ocean (Schlesinger 1997). In the past six decades, inorganic nutrient flux to the ocean has also increased by several times in rivers of the world, particularly in those downstream from agriculture and population centers in the midlatitudes (Turner et al. 2005, Lohrenz et al. 2008). Meybeck (1982, 1993) has provided the most comprehensive estimates of terrestrial fluxes of carbon, nitrogen, and phosphorus (C, N, and P). His flux numbers are essentially confirmed by more recent syntheses (**Table 1**) (Smith & Hollibaugh 1993, Smith et al. 2003, Beusen et al. 2005, Seitzinger et al. 2005). Others

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#### Heterotrophic:

an ecosystem is heterotrophic when it respire more organic carbon than it produces; such a system has a dissolved inorganic carbon/ carbon dioxide excess

#### Coastal zone:

generally includes lower-river basins (<100 km from shore), estuaries, coastal wetlands, and shelves—areas with both land and ocean influences

#### Autotrophic:

an ecosystem is autotrophic when it synthesizes more organic carbon than it respire; such a system has a dissolved inorganic carbon/ carbon dioxide deficit

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**Table 1 Riverine carbon, nitrogen, and phosphorus flux to the global coastal ocean**

Input	Meybeck 1982, 1992	Seitzinger et al. 2005	Smith et al. 2003	Beusen et al. 2005	Adopted here	
					Tmol y <sup>-1</sup>	Tg y <sup>-1</sup>
DIC	32				33.9	407
DIN	0.52	1.8	1.35		1.5	21
DIP	0.03	0.03	0.07		0.05	1.6
DOC	20.5	14	17 <sup>b</sup>		20.5	246
DON	0.85	0.71			0.7	10
DOP	0.027	0.019			0.02	0.6
PIC	14				14	168
POC	18.2		17 <sup>b</sup>	16.4	18	216
PON	2.9			2.1	2.5	35
PP	0.6			0.28	0.4	13
TOC (POC + DOC)	38.5		34 <sup>b</sup>		38.5	462
<b>Autotrophic loading from DIN input and Redfield ratio<sup>a</sup></b>					9.94	119
<b>Autotrophic loading assuming 80% of DIN will be denitrified</b>					1.99	24
<b>Heterotrophic loading (TOC flux)</b>					38.5	462
<b>Heterotrophic loading assuming 70% of land TOC is respired</b>					27.0	323
<b>TOC burial in marine sediment (38.5–27.0 Tmol y<sup>-1</sup>, or 462–323 Tg y<sup>-1</sup>)</b>					11.6	139

<sup>a</sup>The Redfield ratio of 6.6 is used to convert total DIN flux to autotrophic loading.

<sup>b</sup>Data from Smith & Hollibaugh (1993).

Abbreviations: DIC, dissolved inorganic carbon; DIN, dissolved inorganic nitrogen; DIP, dissolved inorganic phosphorus; DOC, dissolved organic carbon; DON, dissolved organic nitrogen; DOP, dissolved organic phosphorus; OC, organic carbon; PIC, particulate inorganic carbon; POC, particulate organic carbon; PON, particulate organic nitrogen; PP, particulate phosphorus; TOC, total organic carbon.

(Duarte & Cebrian 1996, Richey 2004) have suggested higher terrestrial total organic carbon (TOC) flux (650–800 Tg C y<sup>-1</sup>) to the ocean. I will take a more conservative TOC flux of 460 Tg C y<sup>-1</sup> (Tg = 10<sup>12</sup> g), or 38.5 Tmol y<sup>-1</sup> (Tmol = 10<sup>12</sup> mol) for the purpose of discussion in this review.

Let us now examine the net role of terrestrial loadings on ocean metabolism. One may view the TOC loading to the ocean as heterotrophic as its decomposition to CO<sub>2</sub> will drive the oceanic systems toward heterotrophy. Similarly, one may define the dissolved inorganic nitrogen (DIN) flux to the ocean as autotrophic loading because the use of DIN in the ocean by phytoplankton leads to net synthesis of OC and net removal of CO<sub>2</sub>. An examination of **Table 1** suggests that, globally, gross terrestrial heterotrophic loading exceeds that of the autotrophic loading. If we assume that at least 80% of the terrestrial DIN would be denitrified in the ocean margin (Middelburg et al. 1996, Seitzinger et al. 2005), then the terrestrial autotrophic loading is reduced to <2 Tmol y<sup>-1</sup>, with a heterotrophic/autotrophic loading ratio of up to 13–19. Therefore, it is clear that on a global scale, the impact of terrestrial loadings on the ocean is to drive it to a more heterotrophic state, and the large difference in the two loadings suggests a great potential to favor heterotrophy in coastal waters.

## 2.2. Fate of Terrestrial Materials in Ocean Margins

Berner (1989) suggested that most terrestrial OC burial occurs in river deltas at a rate of 114 Tg C y<sup>-1</sup>. In contrast, little OC is buried in open ocean sediments (~6 Tg C y<sup>-1</sup>).

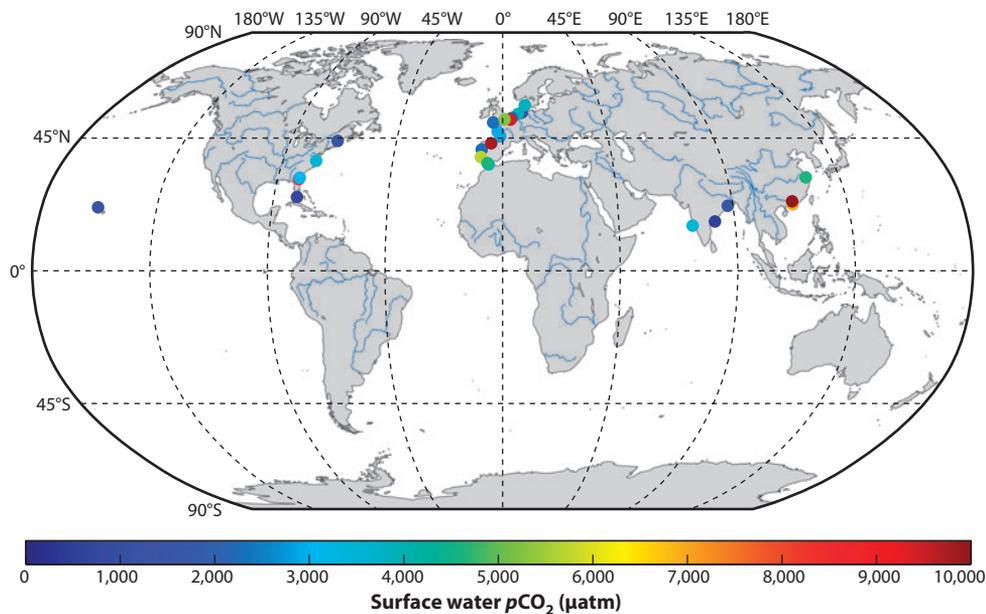
Hedges & Keil (1995), however, suggested that OC burial in nondeltaic shelf sediments is equally as important as that in deltaic sediments (each  $\sim 70 \text{ Tg C y}^{-1}$ ). More recently, Burdige (2007) estimated an additional OC burial of  $70 \text{ Tg C y}^{-1}$  in the 200- to 1,000-m depth range. In summary, among the  $460 \text{ Tg C y}^{-1}$  of OC export, only 25–50% ( $120\text{--}220 \text{ Tg C y}^{-1}$ ) is found in marine sediments. Therefore, one must conclude that most terrestrial OC is respired in sediments and the water column via microbial decomposition. A synthesis of production and respiration rates allowed Smith & Hollibaugh (1993) to conclude that the coastal oceans oxidize approximately 21% of the terrestrial OC loading. Another 47% of the OC loading must be converted to DOC and exported to the open ocean for slow respiration there. However, one must note that there are mismatches in their synthesis as well. First, no system-level production and respiration data from larger river margins were available for their synthesis, although most TOC was carried out to the ocean by large rivers. Smaller rivers often have a high DOC to POC ratio. For example, in the Georgia Bight, 80% of river TOC is DOC (Alberts & Takacs 1999, Moran et al. 1999, Cai et al. 2003b). Thus, it is probably not sufficient to use the net metabolic state derived from such systems to explain the fate of global river OC flux. Second, respiration rate data are extremely scarce in coastal oceans, thus affecting the reliability of these conclusions (Hopkinson & Smith 2005, Jiang et al. 2010). Third, net OC export was viewed as zero in salt marshes in the Smith & Hollibaugh (1993) analysis, and thus OC export from marine vegetated systems was not considered important.

Recently, Duarte et al. (2005) suggested that coastal vegetated ecosystems (e.g., salt marshes, mangroves, etc.) may export a great amount of TOC—on the order of  $0.77\text{--}3.18 \text{ Pg C y}^{-1}$ ;  $\text{Pg} = 10^{15} \text{ g}$ . In this review, I derived a much smaller but still significant OC export flux based on results from the U.S. southeastern marshes ( $0.17\text{--}0.4 \text{ Pg C y}^{-1}$ ; Section 4.4). If proved, this hypothesis (Duarte et al. 2005) could have profound implications for oceanic metabolism and biogeochemistry.

Rivers, however, do not supply freshwater and OC to the ocean evenly along the coastline. Approximately two-thirds of the terrestrial OC is supplied to lower-latitude ( $0\text{--}30^\circ$ ) coastal oceans (see Borges 2005 and figure 5 therein, which was based on data from Ludwig et al. 1996). Low-latitude coastal oceans not only receive more terrestrial OC but may also have higher rates of microbial decomposition at higher annual temperatures (Laws et al. 2000, Price & Sowers 2004, Fuhrman et al. 2008). This view is consistent with the general notion that one may glean from de Haas et al. (2002) that OC is better preserved in cold, high-latitude river deltaic sediments than in warm, low-latitude areas. For example, terrestrial OC burial is  $\sim 50\%$  in the Mackenzie River delta but less than 20% in the Amazon (Showers & Angle 1986, de Haas et al. 2002) and the Mississippi (Cai & Lohrenz 2010) systems. Therefore, it is not unreasonable to speculate that lower-latitude coastal oceans release more  $\text{CO}_2$ . If 75% of the OC delivered to low-latitude coastal oceans is decomposed there, then this alone would generate a  $\text{CO}_2$  flux of  $0.23 \text{ Pg C y}^{-1}$  (i.e.,  $0.46 \text{ Pg C y}^{-1} \times 2/3 \times 75\%$ ; see also Keil et al. 1997 for a similar estimate). If the hypothesis of Duarte et al. (2005) is valid, then even more OC decomposition occurs in low-latitude estuaries and coastal oceans as marine vegetation is largely concentrated in low-latitude areas.

### 3. GLOBAL ESTUARINE $\text{CO}_2$ DEGASSING

Estuarine waters are significant sources of  $\text{CO}_2$  to the atmosphere, with partial pressure of  $\text{CO}_2$  ( $p\text{CO}_2$ ) varying from  $\sim 400\text{--}10,000 \text{ } \mu\text{atm}$  (Figure 2) (Raymond et al. 1997, Cai & Wang 1998, Frankignoulle et al. 1998, Borges 2005, Borges et al. 2006). Therefore, it has been argued that  $\text{CO}_2$  degassing in estuaries could counterbalance the  $\text{CO}_2$  uptake in continental shelves, even though the global surface area of estuaries is only 4% that of the continental shelf (Figure 1).



**Figure 2**

A global distribution of available estuarine  $p\text{CO}_2$  data. Only average  $p\text{CO}_2$  values are plotted, showing that we lack data from the lower latitudes, especially south of the equator. Data sources: Borges (2005), Zhai et al. (2007), Guo et al. (2009), Jiang et al. (2008a), and Chen & Borges (2009); see also Laruelle et al. (2010) for an update. Atmospheric  $p\text{CO}_2$  in coastal zones was approximately 360–385  $\mu\text{atm}$  in year 2000.

Frankignoulle et al. (1998) and Borges et al. (2006) reported that  $\text{CO}_2$  emission from European estuaries (on an average of  $50 \text{ mol m}^{-2} \text{ y}^{-1}$ ) was significant in the regional  $\text{CO}_2$  budget. For example, the regional integrated estuarine  $\text{CO}_2$  efflux ( $\sim 67 \text{ Tg C y}^{-1}$ ) is on the same order of magnitude as the terrestrial biosphere  $\text{CO}_2$  uptake (Janssens et al. 2003) and is equivalent to 5–10% of the total anthropogenic  $\text{CO}_2$  emissions from Western Europe. Borges (2005) and Borges et al. (2005) were the first to compile all available  $\text{CO}_2$  flux data from world estuaries, and they derived a global overall estuarine  $\text{CO}_2$  degassing flux of  $0.34\text{--}0.45 \text{ Pg C y}^{-1}$  (**Figure 1**). This flux is also comparable to the riverine total dissolved inorganic carbon (DIC) flux to the ocean (**Table 1**).

This large estuarine  $\text{CO}_2$  degassing flux seems to suggest that most terrestrial OC must be respired during transport through the estuarine zone. Borges (2005) recognized that this conclusion contradicts OC decomposition studies, which show that only 10–50% of riverine DOC is processed in estuaries (Moran et al. 1999, Raymond & Bauer 2000, Abril et al. 2002). Whereas Chen & Borges (2009) cited the Keil et al. (1997) analysis of the Amazon system and suggested that as much as 70% of riverine POC could be decomposed to provide a sufficient  $\text{CO}_2$  source for estuarine degassing, I suggest that such respiration processes do not occur in the inner estuarine zone for medium to large rivers because of short water transit or residence times. Instead, they must occur largely offshore, especially in shelf sediments (Aller 1998, Aller et al. 2004). Therefore, either the above estuarine  $\text{CO}_2$  degassing rate is greatly overestimated, or it is not supported by riverine OC decomposition.

I suggest that  $\text{CO}_2$  loss from estuaries is supported largely by microbial decomposition of OC produced in coastal wetlands. Cai & Wang (1998) demonstrated that almost all  $\text{CO}_2$  degassing in

the Satilla River estuarine water is supported by lateral transport of DIC produced by microbial respiration in its surrounding salt marshes. They also showed that CO<sub>2</sub> loss to the atmosphere exceeds the river DIC flux by tenfold in the Satilla River estuary. This example might be an extreme case because of the relatively long water residence time (two months) and low alkalinity and DIC content of the water (200–500 μM). Nonetheless, this notion is consistent with the observation in other Georgia River estuaries that essentially all CO<sub>2</sub> produced in the marsh areas and then transported to the estuary is lost to the atmosphere during the estuarine transit, whereas riverine DOC and DIC content are not greatly altered (Cai et al. 1998, Wang & Cai 2004, Jiang et al. 2008a). A similar mechanism was reported for a subestuary of the Chesapeake Bay (Raymond et al. 2000) and for salt marsh estuaries in South Africa (Winter et al. 1996).

Our current knowledge of global estuarine CO<sub>2</sub> efflux is largely uncertain. Several major obstacles prevent us from reliably synthesizing estuarine CO<sub>2</sub> degassing. First, samples have not represented the variety of systems from around the globe adequately enough to support a precise global synthesis (**Figure 2**). Past estuarine CO<sub>2</sub> studies have focused on those estuaries that receive substantial river discharge (Frankignoulle et al. 1998, Borges 2005); much less attention has been given to estuaries that receive little freshwater (Jiang et al. 2008a). An examination of the National Estuarine Inventory Data Atlas (National Ocean Service 1985) suggests that, on the U.S. east coast, the ratio of river-dominated estuaries versus nonriverine estuaries is nearly 1:1. Whereas it is hardly statistically sound to extrapolate it to any other area, this ratio does show that nonriverine estuaries are important geographic features [see also **Figure 4**, which depicts a Geographic Information System (GIS) land cover map]. Moreover, most studies prior to 2005 covered estuaries located largely in the mid- to high latitudes (mostly in Europe) (**Figure 2**). Estuaries in lower latitudes received less study, although the total surface area of low-latitude estuaries is larger than that of mid- and high-latitude estuaries (Borges 2005). Furthermore, large estuaries and large river plumes have not been included in these syntheses. Ironically, CO<sub>2</sub> flux has not been reported for the Chesapeake Bay, which has probably received more research attention than any other large estuary in the United States.

Second, in past studies, diurnal and seasonal changes have been largely ignored. Large diurnal variations in surface *p*CO<sub>2</sub> and air-water CO<sub>2</sub> flux were recently reported in two Chinese estuaries/bays (Dai et al. 2009) and observed in the Neuse River estuary (which enters Pamlico Sound, North Carolina; J. Crosswell and H. Paerl, personal communication).

Third, in reporting surface *p*CO<sub>2</sub> and air-water CO<sub>2</sub> flux, the flux is not always averaged over the estuarine zone. Therefore, a simple mathematical average (as we often use with skewed data sets) would inevitably bias toward the high-*p*CO<sub>2</sub> scenario. In reality, areas with very high CO<sub>2</sub> (generally in the low-salinity section) account for only a small fraction of an estuary (see, e.g., Cai & Wang 1998 for the Satilla and Altamaha River estuaries and Guo et al. 2009 for the Pearl River estuary). I discuss the first obstacle further below.

Borges et al. (2005) calculated that the average CO<sub>2</sub> efflux from low-latitude (0–30°) and mid-latitude (30–60°) estuaries is, respectively, 17 and 46 mol m<sup>-2</sup> y<sup>-1</sup>. However, recent studies showed that CO<sub>2</sub> flux from two large Chinese rivers, the Pearl River estuary in the South China Sea and the inner Changjiang estuary in the East China Sea, was much lower (Zhai et al. 2007, Chen et al. 2008, Guo et al. 2009). A common feature of these larger Chinese rivers, and others such as the Mississippi River (Cai 2003, Cai & Lohrenz 2010), is that they have a high carbonate content in their drainage basins and thus high alkalinity in the river water (Cai et al. 2008). These high-alkalinity rivers are expected to release less CO<sub>2</sub> to the atmosphere. Moreover, CO<sub>2</sub> degassing in these rivers represents only a small loss of their DIC content in the river water or the DIC flux to the ocean. In the Borges (2005) data set, 11 of the 16 systems are high-*p*CO<sub>2</sub> European estuaries. Therefore, the present estimate of global estuarine CO<sub>2</sub> emission may be subject to significant uncertainties

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**River-dominated estuary:** an estuary that has a clear river input and is strongly influenced by river discharge of water and sediments

**Nonriverine estuary:** a coastal water body that is flushed by tidal action and receives minimum freshwater inputs

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because large river estuaries generally have lower  $p\text{CO}_2$  and  $\text{CO}_2$  outgassing flux (except large, low-carbonate, tropical rivers such as the Amazon; Cooley et al. 2007; Cai et al. 2008, 2010).

A detailed study by Jiang et al. (2008a) also showed that  $\text{CO}_2$  efflux in nonriverine estuaries such as coastal lagoons in the southeastern United States have significantly lower  $\text{CO}_2$  than nearby riverine estuaries (Section 4). Jiang et al. (2008a) showed that the annual and area-averaged  $\text{CO}_2$  degassing flux in the Altamaha River estuary was as high as  $36 \text{ mol m}^{-2} \text{ y}^{-1}$ , only moderately lower than the global average given in Borges et al. (2005). In contrast, annual  $\text{CO}_2$  degassing flux in the nearby Sapelo and Doboy sounds was only  $15 \text{ mol m}^{-2} \text{ y}^{-1}$ . Jiang et al. (2008a) were able to show that whereas DIC in the river-dominated estuary is much lower than in the nearby nonriverine estuaries, the amount of  $\text{CO}_2$  that can be released to the atmosphere is higher in the river water. Borges et al. (2006) further suggested that the fraction of riverine  $\text{CO}_2$  in the overall estuarine degassing is related to the flushing rate of the estuary. Fast-transit rivers, like the Altamaha River, have more riverine  $\text{CO}_2$  to ventilate in the estuarine zone than do slow-transit rivers like the Satilla River. I suggest that this is further determined by the carbonate buffer capacity (or alkalinity) of the river water, because low-carbonate rivers have less  $\text{CO}_2$  inventory to offer.

The global estuarine  $\text{CO}_2$  degassing flux estimated in Borges (2005) and Borges et al. (2005) is probably inaccurate (most likely too high) for the above reasons. If we assume that (a) the proportion of the area of the nonriverine estuaries to the total estuaries of the world is the same as that on the eastern coast of the United States and (b) the average extra  $\text{CO}_2$  fluxes of the global riverine estuaries versus nonriverine estuaries are the same as those in coastal Georgia, the air-water  $\text{CO}_2$  fluxes of the global estuaries could be lowered by approximately 25% relative to the Borges et al. (2005) estimate (Jiang et al. 2008a). Thus, I suggest that the global estuarine  $\text{CO}_2$  efflux is approximately  $0.25 \text{ Pg C y}^{-1}$  (Section 4.4). A recent article derived a similar flux using a scaling approach based on a spatially explicit typology of global estuaries (Laruelle et al. 2010). Considering the lower  $p\text{CO}_2$  occurring in large river estuaries and bays, the value may be reduced further. Note that  $\text{CO}_2$  degassing on salt marshes and mangroves is not included in this estimate.

Compounding the issues discussed above, there are also great uncertainties in the global area of estuaries estimated by Woodwell et al. (1973); they derived global estuarine area by extrapolating the ratio of estuarine area to coastline length from the United States to the world. This is a very rough approximation, considering the various distributions of the estuaries of the world. In the meantime, we have to rely on this single product for global synthesis (Borges 2005). This lack of basic area information is unthinkable in today's GIS age. Although there is abundant and detailed GIS information on individual and regional estuaries, there is not a single product that would give us the global estuarine area information, let alone areas of different types of estuaries (but see a recent effort by Dürr et al. 2010).

#### 4. CARBON DYNAMICS IN INTERTIDAL MARSH-ESTUARIES

Intertidal salt marshes in mid- and high latitudes and mangroves in low latitudes are important coastal ecosystems (Weinstein & Kreeger 2000, Gedan et al. 2009). These systems are among the most productive ecosystems on earth (average:  $1,275$ ; range:  $400\text{--}2,250 \text{ g C m}^{-2} \text{ y}^{-1}$ ; Woodwell et al. 1973, Hopkinson 1988) (**Figure 3**).

Using an average marsh net primary production (NPP) rate of  $1,275 \text{ g C m}^{-2} \text{ y}^{-1}$  and the global area (**Figure 1**, caption), we can estimate that globally marsh and mangrove NPP is on the order of  $0.50 \text{ Pg C y}^{-1}$ . Based on an extensive data synthesis, Bouillon et al. (2008) have concluded that global mangrove NPP is approximately  $0.22 \text{ Pg C y}^{-1}$ , which is slightly less than half of the total production. A large part of this NPP is respired within marsh and mangrove systems and some is exported to estuarine waters and the very-nearshore areas. Hopkinson (1988) estimated that the

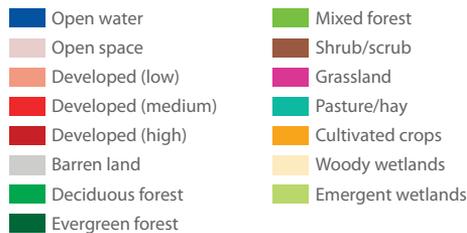
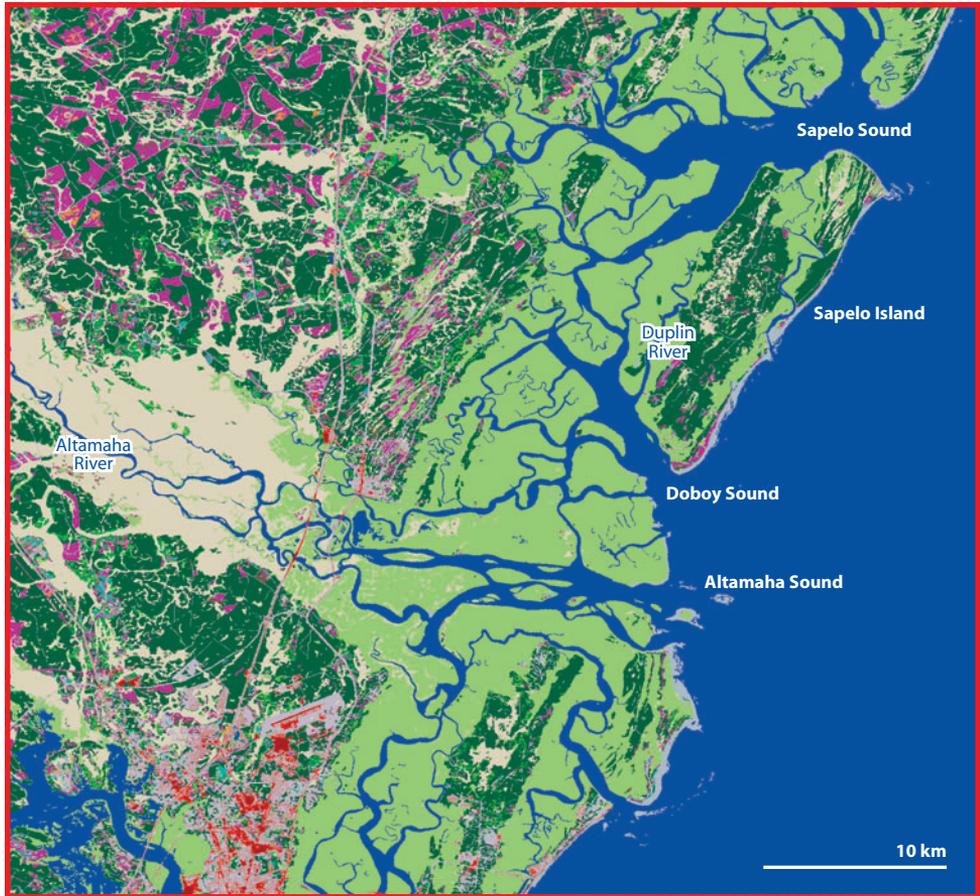


**Figure 3**

Photos of intertidal salt marshes and mangroves. (a) Marshes along a creek on Sapelo Island, taken at a time of high tide during growth season. Courtesy of Melissa Booth. (b) Mangroves in Gazi Bay, Kenya. Courtesy of Alberto Borges. Bouillon et al. (2007) described carbon cycling research at this site.

gross primary production (GPP) in the U.S. southeastern marsh is  $3,941 \text{ g C m}^{-2}\text{y}^{-1}$  with 73% returned to the atmosphere through community respiration. The subject of estuarine respiration has been reviewed by Hopkinson & Smith (2005) and studied by Pomeroy et al. (2000) and Jiang et al. (2010).

A major distinction between marsh and mangrove vegetation and marine plankton is that marsh plants take  $\text{CO}_2$  directly from the atmosphere, and when they die the biomass is released directly



into the water for further decomposition. Thus, marshes and mangroves could potentially form an effective marine carbon sequestration pathway if some OC could escape recycling in coastal systems (Cai et al. 2003b). In today's high-CO<sub>2</sub> world, the strong CO<sub>2</sub> sequestration potential of marshes and mangroves further justifies an extensive measurement of CO<sub>2</sub> and DIC fluxes between the atmosphere, marshes, and adjacent estuaries and a better understanding of the carbon cycling within the estuary-marsh-inner shelf continuum (Andersson & Mackenzie 2004, Duarte et al. 2005, Bouillon et al. 2008).

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**Marsh-dominated estuary:** an estuary that is surrounded by tidal marshes and is strongly influenced by exchanges of materials with the marsh

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#### 4.1. Controls on CO<sub>2</sub> Degassing: A Case Study of Marsh-Estuaries in Georgia

There are abundant intertidal salt marshes along the U.S. southeastern shelf, or South Atlantic Bight (SAB;  $\sim 5.0 \times 10^9$  m<sup>2</sup>). Here, nearly all estuaries, riverine or nonriverine, are surrounded by intertidal freshwater, brackish, and saltwater marshes (Figures 3, 4).

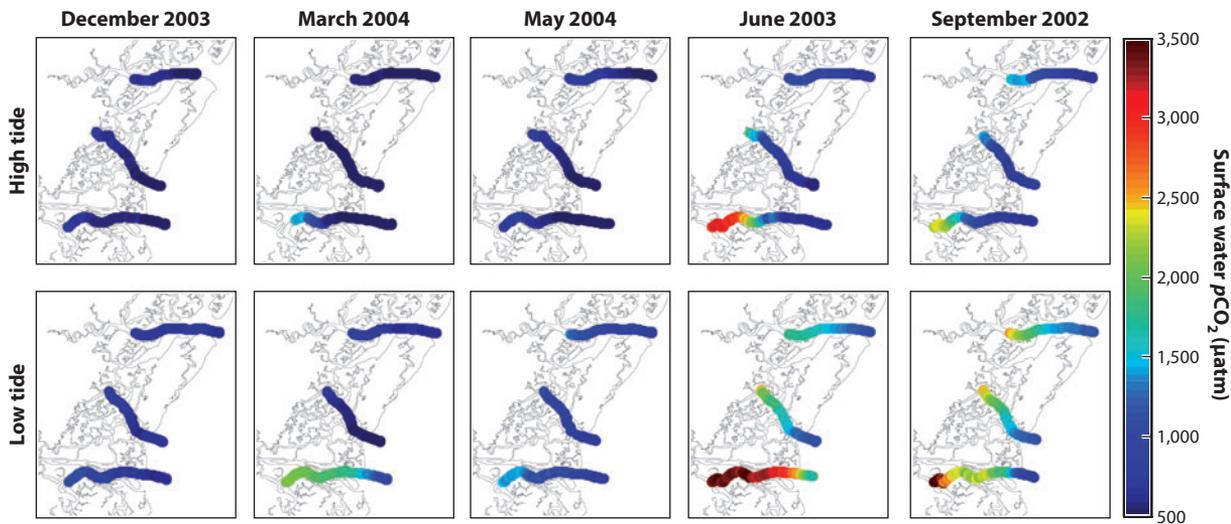
Surface water *p*CO<sub>2</sub> and water DIC were studied in detail at three Georgia Coastal Ecosystem (GCE) Long Term Ecological Research (LTER) sites (Figure 4). It is apparent that there are significant seasonal variations in water *p*CO<sub>2</sub> and DIC in both river-dominated and nonriverine estuaries and marine- and marsh-dominated estuaries (i.e., sounds) in these sites (Figures 5, 6). However, their respective seasonal patterns are quite different. Seasonality of water *p*CO<sub>2</sub> and CO<sub>2</sub> degassing flux in the Altamaha River estuary is controlled by river discharge. In contrast, the seasonal change in CO<sub>2</sub> flux in the marsh-dominated Sapelo and Doboy sounds follows that of the seasonal temperature change, being highest in September, when marsh plants are dying and decomposing, as opposed to early spring when marshes are in a productive stage (Jiang et al. 2008a).

In marsh- or mangrove-influenced estuarine waters, DIC is enriched over the river and ocean mixing line in areas where *p*CO<sub>2</sub> is generally high (Cai & Wang 1998, Raymond et al. 2000, Bouillon et al. 2007). This is particularly true in areas where the marsh-to-open-water ratio is high, such as in the low-salinity zone of the Satilla River, Georgia (Cai & Wang 1998, Cai et al. 2000), or in the high-salinity marshes of Sapelo Sound (Jiang et al. 2008a) and the Duplin River on Sapelo Island (Wang & Cai 2004). In fast-transit rivers like the Altamaha and Savannah rivers (flushing time is typically a few days), this DIC addition or enrichment is not so obvious but is still observable, particularly during low-discharge seasons (fall and early winter) (Figure 6). During the fall and early winter when the marsh organic matter decomposition rate is high, DIC in the low-salinity end of the marsh-surrounded Sapelo and Doboy sounds is even higher than that in seawater (see also Wang & Cai 2004 for the Duplin River) (Figure 6). Although the DIC and salinity relationships differ in the river-dominated estuary (Altamaha Sound) and the marsh-dominated estuaries (Sapelo and Doboy sounds), this seasonal pattern of increased influence of marshes from spring and summer to fall and early winter can be seen in all three

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#### Figure 4

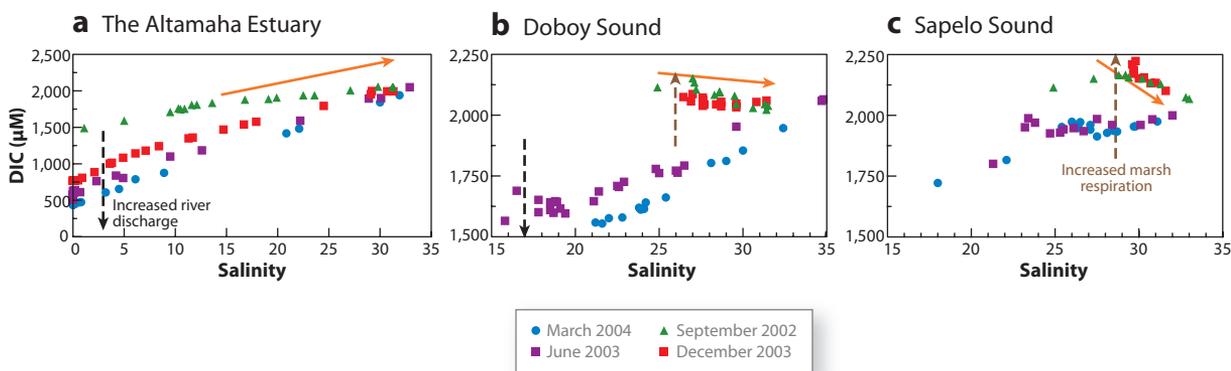
Site map of the Georgia Coastal Ecosystems (GCE) Long-Term Ecological Research (LTER) along the Georgia coast, with Geographic Information System land cover information and extensive coverage of the intertidal marshes (i.e., emergent wetlands) around the river estuary and coastal sounds and the woody wetlands along the tidal lower river. For details of the land cover information, see Homer et al. (2004). Woodwell et al. (1973) also estimated that the ratio of open estuarine water to marsh is 1.75:1 in the South Atlantic Bight. The southernmost study area is a river-dominated estuary (Altamaha Sound); the northernmost area (Sapelo Sound) receives no freshwater input. The middle section (Doboy Sound) receives some freshwater from the Altamaha River, particularly during the high-discharge season. Map created by John Carpenter of GCE-LTER, courtesy of *Natural Earth*, U.S. Natl. Park Service, <http://gce-lter.marsci.uga.edu>.



**Figure 5**

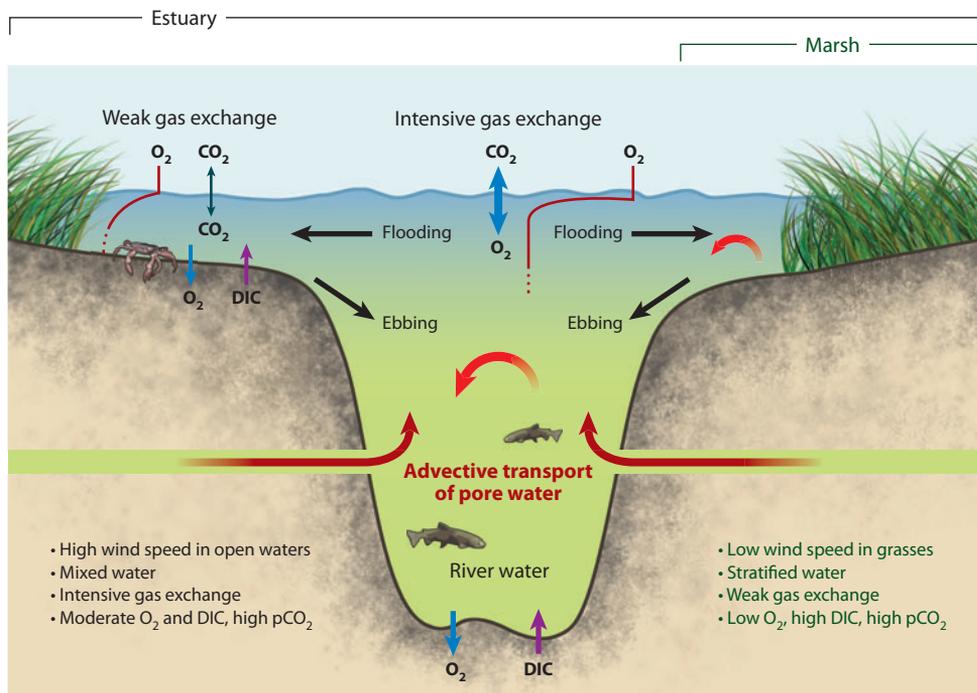
Surface water  $p\text{CO}_2$  distribution at in situ temperature in three Georgia estuaries. See **Figure 4** for details of the sites; see also Jiang et al. 2008a for other relevant information.

systems (**Figure 6**). This is also evident from the fact that  $p\text{CO}_2$  in all three systems is higher during low tides than high tides Jiang et al. 2008a. It was also demonstrated that in the marsh-dominated estuaries, temperature-normalized water  $p\text{CO}_2$  is well correlated with the excess DIC over the river-ocean mixing lines. However, in the river-dominated estuary, the normalized  $p\text{CO}_2$  is not related to excess DIC. Instead, it is correlated to the river discharge, except during the



**Figure 6**

Dissolved inorganic carbon (DIC) versus salinity in the three estuaries along the central Georgia coast (see also Jiang et al. 2008a). Panels (a)–(c) show river-ocean mixing in the Altamaha estuary to nearly no river influence in Sapelo Sound. The downward black arrow indicates increased river discharge in spring and early summer, whereas the upward brown arrow indicates increased marsh respiration in fall and early winter. The orange arrows indicate a changing pattern in fall and early winter from full river-ocean mixing with some marsh input (data curves are concave upward) in the Altamaha estuary (*upward orange arrow*) to marsh-ocean mixing with very little river component (due to less river discharge) in Sapelo Sound, which has a higher DIC than the seawater (*downward orange arrow*).



**Figure 7**

A conceptual model of gas exchange in the marsh-estuarine complex. This vertical profile shows the transport of respiration signals from intertidal marshes into the main estuarine channel. Expected  $O_2$  concentration profiles are also presented for estuarine and marsh waters, respectively (modified from Cai et al. 1999). A key point proposed by Cai et al. (1999) has to do with the ratio of marsh to open-water area and the ratio of the main channel water depth versus that of the marshes; e.g., for the same water-to-air  $pCO_2$  difference ( $\Delta pCO_2$ ), a 4-m water column in the main channel could support a  $CO_2$  degassing rate eight times that of a 0.5-m water column over the marshes. Groundwater is another source of dissolved inorganic carbon (DIC) to the coastal creeks (Cai et al. 2003a; Moore 2007, 2010). Bright red arrows represent microbial decomposition of organic matter.

low-discharge and high-marsh-respiration season of September when the marsh signal is also clearly observed (Jiang et al. 2008a).

What supports the very high  $CO_2$  degassing and DIC export flux in marsh-dominated estuaries? The depth-integrated microbial decomposition rate in the main river channel is generally much lower than the air-water  $O_2$  and  $CO_2$  flux (Cai et al. 1999, Pomeroy et al. 2000). I have hypothesized that such high gas flux in marsh-surrounded estuaries is largely supported by microbial decomposition of organic carbon from the surrounding intertidal salt marshes (Figure 7). The microbial metabolic signals (low  $O_2$  and high  $pCO_2$ ) are “kept” in marsh waters due to low gas exchange rates because of low wind conditions in vegetated areas. When this water is brought into the main channel by tidal excursion and advective flow from sediments, gas exchange can occur freely. Such gas exchange flux can be several times the local depth-integrated metabolic rate as it is supported by nonlocal, lateral transport. This relationship was shown to apply well in estuaries with long water residence times (i.e., the Satilla and Ogeechee rivers) but not as well for fast-transit rivers with a short estuarine flushing time (i.e., the Altamaha and Savannah rivers) in Georgia (Cai et al. 1999).

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**Benthic:** properties and biogeochemical processes related to the sediments of an aquatic system

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Similarly, in the marsh-dominated Duplin River on Sapelo Island, the upper stream water during low tides was essentially all marsh waters that had been over the marshes during the high tides. Therefore, CO<sub>2</sub> degassing and creek water DIC in excess of the river-ocean mixing line are a result of net marsh heterotrophy. This marsh water net heterotrophy has a clear seasonal pattern with low value during the marsh production season (spring) and high value during the marsh decomposition season (fall; Wang & Cai 2004). This mechanism of CO<sub>2</sub> production in salt marshes and export as DIC to creeks/rivers followed by release into the atmosphere also operates in intertidal mangrove estuaries (Bouillon et al. 2007, 2008).

## 4.2. Rate of Dissolved Inorganic Carbon Export from Intertidal Marshes

Based on seasonal DIC monitoring over six stations in the Duplin River and a previous hydrodynamic study, Wang & Cai (2004) estimated that DIC export from the Sapelo Island marshes is on the order of 156 g C m<sup>-2</sup>y<sup>-1</sup>. This marsh DIC export rate is comparable to the estimate for a salt marsh in North Inlet, South Carolina (Morris & Whiting 1986), and for tidal freshwater marshes in Virginia (Neubauer & Anderson 2003). Extrapolating this flux to the entire SAB, a total flux of 0.7 Tg C y<sup>-1</sup> is derived.

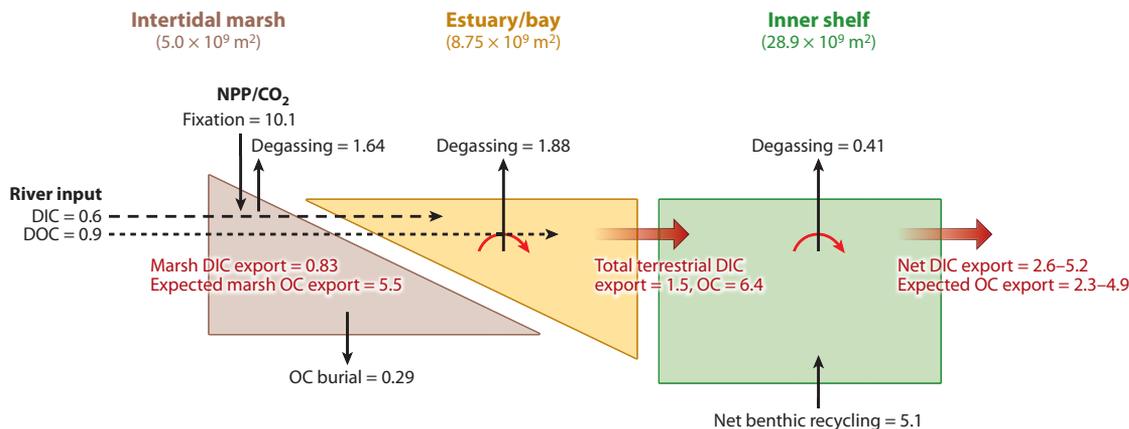
Based on an indirect method (ratio to DOC), Bouillon et al. (2008) estimated that DIC export rate in mangroves could be as high as 1,100 g C m<sup>-2</sup>y<sup>-1</sup> (or 178 Tg C y<sup>-1</sup> globally). These authors suggested that the benthic remineralization and subsequent DIC export could account for nearly 50% of the mangrove net primary production.

## 4.3. Marsh Organic Carbon Accumulation

Globally, the rate of sea level rise (SLR) is approximately 1.5–3.1 mm y<sup>-1</sup> (FitzGerald et al. 2008). The vertical accretion rates in the U.S. southeastern marshes range from 2 mm y<sup>-1</sup> for salt marshes to 4–6 mm y<sup>-1</sup> for brackish and tidal freshwater marshes (Craft 2007), indicating that they have been able to keep pace with SLR (2.5 mm y<sup>-1</sup> in this area; Craft et al. 2007) by trapping sediment and accumulating soil organic matter. Loomis & Graft (2010) recently measured cesium-137 (<sup>137</sup>Cs) accretion rates along three river-dominated estuaries in Georgia as 1.9 and 4.4 mm y<sup>-1</sup>, respectively, for salt and brackish marshes. These accretion rates correspond to OC accumulation rates of 40 and 124 g C m<sup>-2</sup>y<sup>-1</sup>, respectively. Based on their data, I derived an average OC accumulation rate of 57 g C m<sup>-2</sup>y<sup>-1</sup>. Extrapolating this value for the entire SAB, an SAB marsh OC accumulation rate of 0.29 Tg C y<sup>-1</sup> was derived. Assuming this value applies globally to all marshes and mangroves (total area = 0.38 × 10<sup>12</sup> m<sup>2</sup>), a global marsh and mangrove OC burial rate is 22 Tg C y<sup>-1</sup>. This is much lower than the value derived by Duarte et al. (2005), who obtained a total accumulation of 84 Tg C y<sup>-1</sup> for marsh and mangrove sediments. However, Duarte et al. (2005) double-counted the marsh area as 0.4 × 10<sup>12</sup> m<sup>2</sup>, in addition to a mangrove area of 0.2 × 10<sup>12</sup> m<sup>2</sup>, and used a higher accumulation rate of 139–151 g C m<sup>-2</sup>y<sup>-1</sup>. If we accept the higher mangrove OC accumulation rate (18.4 Tg C y<sup>-1</sup>, from Bouillon et al. 2008) and calculate marsh OC accumulation (12.5 Tg C y<sup>-1</sup>) separately, then the total marsh and mangrove OC accumulation rate is 31 Tg C y<sup>-1</sup>, which is still quite a bit lower than that of Duarte et al. (2005).

## 4.4. Overall Carbon Budget in Marsh-Estuary Systems and Coastal Metabolism

Based on the above discussion of various carbon flux terms, I present a conceptual carbon transport model and a mass balance analysis for a river-marsh-estuary-inner shelf continuum scaled up to the entire U.S. southeastern marsh (Figure 8). Although the numbers may change as we learn more



**Figure 8**

Carbon transport model and mass balance analysis for a marsh-estuarine-inner shelf continuum scaled up to the entire South Atlantic Bight (SAB; modified from Cai et al. 2003b). Units are in  $10^{12} \text{ g C y}^{-1}$  (or  $\text{Tg C y}^{-1}$ ). The total marsh area is  $5.0 \times 10^9 \text{ m}^2$  according to Reimold (1977) and Woodwell et al. (1973). The open estuarine water-to-marsh ratio (1.75:1) of Woodwell et al. (1973) is used to estimate the open-water area. Total riverine export of inorganic carbon to the SAB is from Cai & Wang (1998). Riverine organic carbon (OC) flux is estimated based on an average dissolved organic carbon (DOC) concentration of  $10 \text{ g C m}^{-3}$ , a 20% particulate organic carbon (POC)-to-DOC ratio (Alberts & Takacs 1999, Moran et al. 1999, Cai et al. 2003b), and a total river discharge rate of  $75 \text{ km}^3$  (Atkinson et al. 1978, Menzel 1993). Bright red arrows represent microbial decomposition of organic matter. The total salt marsh carbon fixation estimate of  $10.1 \text{ Tg C y}^{-1}$  is based on a net primary production (NPP) of the salt marshes of  $2,025 \text{ g C m}^{-2} \text{ y}^{-1}$  (Hopkinson 1988).  $\text{CO}_2$  degassing from marsh and creek waters is estimated from the Duplin River study (Wang & Cai 2004) and that from the exposed marsh during low tides is from the North Inlet (South Carolina) study (Morris & Whiting 1986).  $\text{CO}_2$  degassing from open estuarine and bay waters is from the study in Sapelo, Doboy, and Altamaha sounds (Jiang et al. 2008a). Dissolved inorganic carbon (DIC) export rates from marshes to estuaries/bays are based on an average value from the Duplin River and North Inlet (Section 4.2).  $\text{CO}_2$  degassing from the inner shelf zone is from Jiang et al. (2008b). DIC export to the outer shelf was estimated as  $2.6 \text{ Tg C y}^{-1}$  if the shelf water residence time is 3 months (Atkinson et al. 1978, Cai et al. 2003b) or  $5.2 \text{ Tg C y}^{-1}$  if it is 1.5 months (Moore 2007). Net benthic recycling flux of DIC is based on the difference between benthic respiration rate (Jahnke et al. 2000) and benthic primary production (Jahnke et al. 2008).

about this or other systems, the general concept should hold.  $\text{CO}_2$  degassing over marsh waters is the least known part of the carbon budget as we have no field measurements. The tower-based eddy correlation method, however, may rapidly improve our knowledge in this area (Kathilankal et al. 2008).

Bearing in mind that this budget estimate is highly uncertain due to our limited knowledge, I reach the following conclusions regarding coastal  $\text{CO}_2$  and OC dynamics.

1. If the  $\text{CO}_2$  efflux in the open estuarine areas is scaled up to the globe, we derive a global estuarine  $\text{CO}_2$  degassing flux of  $226 \text{ Tg C y}^{-1}$ —essentially the same as that derived in Section 3.
2. The aquatic part of the marsh-estuarine system is highly heterotrophic, driven by net autotrophy of the marsh plants. From  $\text{CO}_2$  degassing and DIC export, 44% of marsh NPP is respired within this system, which is consistent with an earlier estimate based on the OC budget (Hopkinson 1988).
3. Expected OC export from the marsh, estimated as total NPP less degassing, DIC export, and OC burial ( $=10.1 - 4.36 - 0.29 = 5.5 \text{ Tg C y}^{-1}$ ), is 54% of NPP. Assuming most river DOC goes to the shelf directly without significant decomposition (Hopkinson 1988), then the total OC export from marshes and rivers to the SAB is  $6.4 \text{ Tg C y}^{-1}$ .

4. From the mass balance, inner-shelf pelagic net ecosystem production (NEP) is  $3.6 \text{ Tg C y}^{-1}$  (i.e.,  $1.5 + 5.1 - 0.41 - 2.6$ ) if the offshore DIC flux to the ocean is  $2.6 \text{ Tg C y}^{-1}$  or  $1.0 \text{ Tg C y}^{-1}$  if the DIC flux is  $5.2 \text{ Tg C y}^{-1}$ . Although the water column is autotrophic, the whole inner-shelf system is heterotrophic, and the system  $\text{NEP} = 1.5 - 0.41 - 2.6 = -1.5$ , or  $-4.1 \text{ Tg C y}^{-1}$ . Depending on how well we know the offshore DIC flux, a significant part of the marsh-exported OC will be respired in the inner shelf sediments. It is emphasized here that the inner-shelf benthic system is highly heterotrophic, recycling most of the marsh-exported OC. Jahnke et al. (2000) reported a very high benthic primary production (BPP) rate together with a high respiration rate. It was found later that the BPP rate is much lower than the earlier estimate due to low light availability at the seafloor, during storms in particular (Jahnke et al. 2008), and is less than 10% of the benthic respiration in the inner shelf.
5. Offshore DIC export flux,  $2.6\text{--}5.2 \text{ Tg C y}^{-1}$ , exceeds the river DIC flux greatly, as a result of decomposition of marsh biomass.
6. Finally, OC export to the outer shelf or possibly to the open ocean is between  $2.3\text{--}4.9 \text{ Tg C y}^{-1}$  (i.e., total marsh plus river OC export less inner-shelf NEP). If we scale this up to the global margin by using the ratio of SAB marsh to the global area (i.e.,  $5 \times 10^9 \text{ m}^2$  versus  $0.38 \times 10^{12} \text{ m}^2$ ), we derive a global OC export to the outer shelf and possibly the open ocean as  $174\text{--}400 \text{ Tg C y}^{-1}$ . Whereas this is much lower than that ( $0.77\text{--}3.18 \text{ Pg C y}^{-1}$ ) estimated by Duarte et al. (2005), it is indeed a significant number compared with the global riverine OC flux ( $460 \text{ Tg C y}^{-1}$ ) or oceanic OC burial rate ( $120\text{--}220 \text{ Tg C y}^{-1}$ ). The fate of this OC is unknown either on the U.S. east coast or in other margins; however, it must contribute to the ocean carbon cycling and budget.

## 5. CONTINENTAL SHELF $\text{CO}_2$ FLUX

Tsunogai et al. (1999) and Thomas et al. (2004) drew attention to the importance of continental shelf  $\text{CO}_2$  uptake by suggesting that continental shelves may absorb atmospheric  $\text{CO}_2$  by up to  $0.4\text{--}1.0 \text{ Pg C y}^{-1}$ , or 20–50% of known open ocean uptake at the time ( $2.0 \text{ Pg C y}^{-1}$ ). However, these earlier estimates have been based largely on data from a single type of shelf located in the northern temperate zone near populated areas (Ducklow & McCallister 2004). The vast majority of other shelves was ignored (Cai & Dai 2004, Cai et al. 2006). Using all available continental shelf sea-air  $\text{CO}_2$  flux data and a scaling method, Borges and colleagues (Borges 2005, Borges et al. 2005, Chen & Borges 2009) derived a global continental shelf sea-air  $\text{CO}_2$  flux between 0.3 and  $0.4 \text{ Pg C y}^{-1}$  (Figure 1). It is clear from these compilations that continental shelves, especially low-latitude shelves, are greatly undersampled (Cai et al. 2006).

Cai et al. (2006) divided the coastal ocean into three major types (polar, western boundary current, and eastern boundary current shelves) and seven provinces and synthesized  $\text{CO}_2$  flux in individual provinces. Following this approach and using an updated database, I estimated net global continental shelf  $\text{CO}_2$  uptake flux to be  $0.24 \text{ Tg C y}^{-1}$  (Figure 9). The updates include a large increase in the Arctic  $\text{CO}_2$  uptake according to Bates & Mathis (2009) and a slight reduction in low-latitude  $\text{CO}_2$  release according to Jiang et al. (2008b). My global net flux is still somewhat lower than a recent estimate ( $0.37 \text{ Pg C y}^{-1}$ ) by Chen & Borges (2009) but agrees well with another recent study that used a different scaling method (Laruelle et al. 2010).

A striking latitudinal contrast in shelf sea-air  $\text{CO}_2$  flux also emerges from this analysis. Present-day shelves located between  $30^\circ$  and  $90^\circ$  are sinks of atmospheric  $\text{CO}_2$  with a total air-to-sea flux of  $0.35 \text{ Pg C y}^{-1}$ . In contrast, those shelves located from  $0^\circ$  to  $30^\circ$  are sources of  $\text{CO}_2$  to the atmosphere, with a total release of  $0.10 \text{ Pg C y}^{-1}$ .

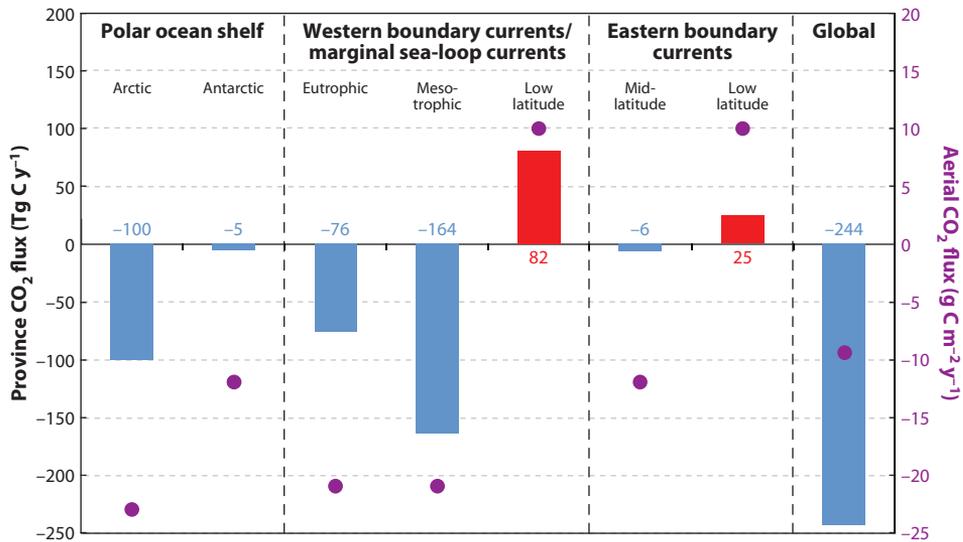


Figure 9

Air-sea CO<sub>2</sub> flux in various continental shelf provinces. Purple circles indicate aerial CO<sub>2</sub> flux, and vertical bars are province CO<sub>2</sub> flux. Blue bars indicate CO<sub>2</sub> uptake by the shelf province and red bars, release. The seven provinces are (left to right): Arctic, Antarctic, eutrophic, mesotrophic, low-latitude western boundary current, and mid- and low-latitude eastern boundary current (Walsh 1988). The “Global” blue bar represents a net sum of all of these provinces. See Cai et al. (2006) for the oceanographic features and CO<sub>2</sub> behaviors of these provinces.

The range of continental shelf CO<sub>2</sub> uptake of 0.2–0.4 Pg C y<sup>-1</sup> appears to contradict the general consensus that approximately 0.5 Pg C is exported annually from the land to the ocean margin and a large part is respired there (Section 2). Mackenzie et al. (2004) and Ducklow & McCallister (2004) suggested that this was probably due to the anthropogenic increase of CO<sub>2</sub> in the atmosphere. However, studies in the North Sea (Thomas et al. 2007) and the South China Sea (Tseng et al. 2007) suggested that in these large marginal seas, sea surface *p*CO<sub>2</sub> follows that of atmospheric increases relatively well. A comparison of our recent study in the U.S. southeastern shelf (Jiang et al. 2008b) with historical records indicates that wintertime surface *p*CO<sub>2</sub> did not change between 1995 and 2005 (W-J Cai, unpublished results; original data at [http://cdiac.ornl.gov/oceans/global\\_pco2.html](http://cdiac.ornl.gov/oceans/global_pco2.html)). I suggest that this difference is determined by surface water residence time, which is less than three months in the SAB but is one to several years in large marginal seas. In most shelves, water residence time is less than a few months and is shorter than or similar to the characteristic time of air-sea CO<sub>2</sub> exchange (Sarmiento & Gruber 2006). Therefore, I suggest that in most shelves, sea surface *p*CO<sub>2</sub> does not follow the atmospheric CO<sub>2</sub> increase well, and this delay leads to the large CO<sub>2</sub> uptake today, even though the shelves overall are heterotrophic and produce CO<sub>2</sub>.

Let us first consider a scenario in the year 1900 with atmospheric *p*CO<sub>2</sub> at approximately 285 μatm and an assumed global average shelf sea-surface *p*CO<sub>2</sub> at 320 μatm. Using a CO<sub>2</sub> gas transfer velocity of 12 cm h<sup>-1</sup>, a CO<sub>2</sub> flux of 3.4 mmol m<sup>-2</sup> d<sup>-1</sup> is estimated, which leads to a global shelf CO<sub>2</sub> degassing flux of 0.38 Pg C y<sup>-1</sup> (total shelf area = 25.8 × 10<sup>12</sup> m<sup>2</sup>). However, with an average global *p*CO<sub>2</sub> at approximately 360 μatm in the year 2000, if we assume a global average shelf seawater *p*CO<sub>2</sub> at 340 μatm, we derive a shelf CO<sub>2</sub> exchange flux of -1.9 mmol m<sup>-2</sup> d<sup>-1</sup> or -0.22 Pg C y<sup>-1</sup>. Therefore, a large increase of 75 μatm in the atmospheric *p*CO<sub>2</sub> and a small

increase of  $20 \mu\text{atm}$  in the surface seawater  $p\text{CO}_2$  over the last century would turn a coastal ocean that is a  $\text{CO}_2$  source of  $0.38 \text{ Pg C y}^{-1}$  into a sink of  $0.22 \text{ Pg C y}^{-1}$ . The above postulation explains why heterotrophic shelves can be a  $\text{CO}_2$  sink today. If proved to be true, then, this reverse of shelf air-sea  $\text{CO}_2$  flux would imply that shelf export of DIC to the open ocean has also increased over the past century on the order of  $0.6 \text{ Pg C y}^{-1}$ .

### SUMMARY POINTS

1. Estuarine waters are a significant source of  $\text{CO}_2$  to the atmosphere, with a global efflux of  $0.25 \pm 0.25 \text{ Pg C y}^{-1}$ . This degassing is largely supported by the respiration of salt-marsh and mangrove biomass. Therefore, the entire marsh-estuarine system, including vegetation, must be a sink of atmospheric  $\text{CO}_2$ . A significant part of the marsh-derived OC would survive the estuarine and nearshore recycling and escape to the outer shelf, slope, and the open ocean for further recycling or burial.
2. Terrestrial OC carried by rivers, particularly large and fast-transit rivers, escapes estuarine decomposition and contributes to respiration in ocean margins and interiors. The observed contemporary  $\text{CO}_2$  uptake in mid- to high-latitude continental shelves ( $0.35 \text{ Pg C y}^{-1}$ ) is driven largely by increases in atmospheric  $\text{CO}_2$  concentration. This change of physical driving force also weakens the  $\text{CO}_2$  release from lower-latitude ocean margins ( $0.10 \text{ Pg C y}^{-1}$ ), where most of the riverine OC is delivered and respired. Thus, continental shelves are sites of terrestrial OC degradation/incineration but are a  $\text{CO}_2$  sink ( $0.25 \pm 0.25 \text{ Pg C y}^{-1}$ ) for the atmosphere.
3. Although the importance of  $\text{CO}_2$  flux and carbon budget in the land-ocean margin is indisputable, and we know  $\text{CO}_2$  fluxes relatively well for some coastal water components, our current knowledge of  $\text{CO}_2$  flux in coastal zones is still insufficient to derive precise information for climate change prediction (i.e., flux within  $\pm 0.05 \text{ Pg C y}^{-1}$ ).

### FUTURE ISSUES

1. Spatial and temporal coverage in both estuarine and shelf  $\text{CO}_2$  flux research must be further improved, although we have witnessed a great improvement in the past 5 to 10 years. Information at the boundary of estuaries and inner shelves (i.e., the nearshore areas) is often missing in our current studies as large ocean vessels have difficulty reaching these areas.
2. To improve the accuracy of global synthesis of estuarine  $\text{CO}_2$  flux and carbon budget, better estimates of the global area of estuaries as well as areas of various types of estuaries are critical.
3. We know little about the  $\text{CO}_2$  release rates from marsh waters and soils, nor do we have a good understanding of the amount of  $\text{CO}_2$  fixation in marsh and mangrove biomass. New technologies such as tower-based eddy correlation observations should be applied to these highly heterogeneous areas together with more traditional survey methods.

4. Integrated research following the footprint of carbon from terrestrial systems and watersheds to rivers, to coastal systems, and further to the open oceans, with the focus on estuarine-marsh-shelf hot spots, must be carried out free of the traditional field or disciplinary limitations.
5. The contribution of salt marsh- and mangrove-derived DIC and OC to estuarine and shelf CO<sub>2</sub> flux, as well as their contribution to other larger oceanic CO<sub>2</sub> cycling issues, should be isolated from those of riverine OC. This effort will help us to understand the processes/mechanisms controlling ocean margin carbon cycling and related issues such as the formation of coastal hypoxia.

## DISCLOSURE STATEMENT

The author is not aware of any affiliations, memberships, funding, or financial holdings that might be perceived as affecting the objectivity of this review.

## ACKNOWLEDGMENTS

I would like to thank S. Smith, C. Hopkinson, J. Bauer, M. Dai, C. Craft, and S. Lohrenz for discussions. My former students Z. Wang, L. Jiang, F. Chen, X. Guo, and J. Hartmann are acknowledged for their contributions. I am grateful to my colleague Yongchen Wang for taking care of the lab and fieldwork. Finally, I thank Cindy Lee and the Marine Science editorial committee for inviting me to write this article. Financial support for my coastal zone carbon research has been provided by the National Science Foundation, National Aeronautics and Space Administration, and the National Oceanic and Atmospheric Administration.

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## Errata

An online log of corrections to *Annual Review of Marine Science* articles may be found at <http://marine.annualreviews.org/errata.shtml>