Influence of terrestrial inputs on continental shelf carbon dioxide

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Abstract

Air-sea carbon dioxide (CO$_2$) fluxes have recently been reported for the US South Atlantic Bight (SAB), a low-latitude shallow continental shelf bordered landward by abundant salt marshes and rivers. In this study, influences of terrestrial inputs on sea surface partial pressure of CO$_2$ ($p$CO$_2$) in the SAB are quantified. After removing $p$CO$_2$ variations due to the annual temperature cycle and air-sea gas exchange from the in situ $p$CO$_2$, temperature and gas exchange corrected (TG-corrected) $p$CO$_2$ is derived. Contributions from the river, marsh, and continental shelf to the TG-corrected $p$CO$_2$ are then calculated. Findings show that CO$_2$ contributions from the river [$\Delta p$CO$_2$(river)] are highest close to the coast and decrease with distance offshore. For example, $\Delta p$CO$_2$(river) was up to 30 µatm on the inner shelf but averaged only 0–3 µatm on the outer shelf during January and March 2005. CO$_2$ contributions from salt marshes [$\Delta p$CO$_2$(marsh)] show similar spatial and seasonal distributions as $\Delta p$CO$_2$(river), with the magnitude of $\Delta p$CO$_2$(marsh) being about three times as high as that of $\Delta p$CO$_2$(river). CO$_2$ contributions from within the shelf [$\Delta p$CO$_2$(shelf)] are highest among the three components. Compared to $\Delta p$CO$_2$(river) and $\Delta p$CO$_2$(marsh), $\Delta p$CO$_2$(shelf) show the smallest onshore-offshore gradients. Despite large uncertainties, this study clearly demonstrates the importance of terrestrial impacts on coastal ocean CO$_2$ distribution.

1 Introduction

By linking the land, ocean, and atmosphere, continental shelves play a key role in the global carbon cycle (Mackenzie, 1991; Smith and Hollibaugh, 1993). Despite their small surface areas (7–8 % of the global ocean surface area), continental shelves sustain disproportionately high levels of primary production, remineralization, and organic carbon burial (Walsh, 1988; Wollast, 1993; Gattuso et al., 1998; de Hass et al., 2002). Recent studies have shown that global continental shelves are an important sink of...
atmospheric carbon dioxide (CO$_2$). The “continental shelf pump”, which was originally proposed by Tsunogai et al. (1999), takes up CO$_2$ from the atmosphere at a rate of 0.2–1.0 Gt C each year (Tsunogai et al., 1999; Borges et al., 2005; Cai et al., 2006; Chen and Borges, 2009; Cai 2011). Fluxes of this magnitude account for about 15–70% of the current estimate of CO$_2$ uptake by the open ocean (1.2–1.6 Pg C yr$^{-1}$) (Takahashi et al., 2009), thus representing a significant portion of the oceanic uptake of CO$_2$.

Based on influences from land and the open ocean, most continental shelves, in particular those that are aligned with a western boundary current and have a wide shelf (Cai et al., 2006), can be divided into two zones: the proximal shelf (i.e., inner) that is strongly impacted by land, and the distal (i.e., middle and outer) shelf that is mainly affected by the open ocean (Rabouille et al., 2001). Compared to the distal shelf, the proximal shelf usually shows much steeper biogeochemical gradients. Therefore, higher resolution surveys are warranted to understand the biogeochemical processes on the proximal shelf. Unfortunately, the proximal shelf has often been neglected by continental shelf CO$_2$ studies, partly due to navigational or geopolitical reasons. Tsunogai et al. (1999), for example, estimated a global “continental shelf pump” of 1.0 Gt C yr$^{-1}$ based on their surveys in the East China Sea (ECS), but did not cover the proximal ECS along the Chinese coast (Xue et al., 2011).

Continental shelves are strongly impacted by nutrients from land (Thomas et al., 2004). As a result, proximal continental shelves usually sustain a relatively high level of biological productivity (Walsh, 1988; Wollast, 1993), which may draw down CO$_2$. However, this effect may be counteracted by enhanced heterotrophic activity supported by organic carbon input from land (Smith and Hollibaugh, 1993). In addition, direct inorganic carbon input from river water plays an important role in enhancing $p$CO$_2$ of shelf waters (Raymond et al., 2000; Borges et al., 2006; Jiang et al., 2008b). Tidal exchange with intertidal marshes (Wang and Cai, 2004) and mangroves (Borges et al., 2003) may also raise $p$CO$_2$ in continental shelf waters.

The South Atlantic Bight (SAB) off the Southeastern United States is a low-latitude shallow continental shelf bordered landward by abundant salt marshes and freshwater
discharge and seaward by a western boundary current, the Gulf Stream. A recent study has shown that while the distal SAB shelf is an atmospheric CO\textsubscript{2} sink of \(-1.3\) mol m\(^{-2}\) yr\(^{-1}\), the proximal SAB shelf is a source of \(1.2\) mol m\(^{-2}\) yr\(^{-1}\) (Jiang et al., 2008a). The goal of this study is to estimate how the annual temperature cycle, air-sea gas exchange, input from rivers, salt marshes, and within shelf water control sea surface \(p\text{CO}_2\) in this region.

2 Study site and methods

2.1 Site description

The SAB continental shelf is \(\sim10–15\) m deep inshore and 50–75 m deep at the shelf break (Fig. 1). The Gulf Stream flows northward along the shelf break. The shorelines of Georgia and South Carolina are characterized by extensive salt marshes (3000 km\(^2\), Alexander et al., 1986). Tidal currents flood and drain intertidal salt marshes twice daily and transport materials between the marshes and the SAB (Hopkinson, 1985). Most rivers in this region are located in the central and northern part of the shelf. Discharge usually peaks in February–April, and a secondary peak may occur in fall, with a total annual discharge of about 66 km\(^3\) (~2.7% of the SAB volume) (Menzel, 1993). Groundwater may also represent important additional inputs of water and other materials to the shelf waters (Moore, 2007 and references therein).

A Coastal Frontal Zone (CFZ), formed by a pressure gradient induced by freshwater discharge frequently occurs at 10–30 m isobath about 10–30 km offshore on the SAB shelf (Blanton, 1981). CFZ presents a dynamic barrier to the seaward transport of materials (Blanton and Atkinson, 1983). For simplicity, we refer to the shelf shoreward the CFZ as the proximal SAB (roughly equivalent to the inner shelf), and the shelf seaward the CFZ as the distal SAB (roughly equivalent to the middle and outer shelf). The proximal SAB is turbid as a result of material transport from rivers and exchange with intertidal salt marshes (Pomeroy et al., 2000). Primary production here is mainly
driven by nutrients recycled in the water column (Dunstan and Atkinson, 1976; Hanson et al., 1990) and from sediments (Jahnke et al., 2005). On the distal SAB shelf, water clarity increases dramatically, and the euphotic zone extends to the seafloor (Nelson et al., 1999). Production here is strongly influenced by intrusions induced by Gulf Stream frontal eddies (Atkinson et al., 1984).

2.2 Sampling

A whole-shelf survey consisting of five onshore-offshore transects (A-, B-, C-, D-, and E-transects from south to north, Fig. 1) was carried out in the SAB during six cruises: 05–16 January 2005, 19–30 March 2005, 27 July–5 August 2005, 7–17 October 2005, 16–21 December 2005, and 17–27 May 2006. Surface water $pCO_2$, temperature, salinity, and atmospheric pressure at sea level were measured while underway during all cruises (Jiang et al., 2008a). Dissolved inorganic carbon (DIC) was sampled on all five transects except for December 2005, when only E-, C-, and A-transects were covered. Dissolved organic carbon (DOC) samples were collected on D-, C-, and B-transects during January, March, and October 2005, and on all 5 transects during May 2006.

2.3 Sample analysis

DIC concentration was measured using an infrared $CO_2$ detector-based DIC analyzer with a precision of 0.1% (Wang and Cai, 2004). DOC samples collected during the cruises of March, July, and October 2005 were measured at the Radiocarbon Laboratory of Virginia Institute of Marine Science (VIMS) using a Shimadzu TOC-5000A high-temperature Pt-catalyzed analyzer with a mean analytical error of 1.4 $\mu$mol l$^{-1}$ (DeAlteris, 2007). DOC samples from May 2006 were analyzed in W. L. Miller’s lab (University of Georgia) using a Shimadzu TOC-VCPN analyzer. Reference standards (deep Sargasso Sea seawater from D. A. Hansell’s group at the University of Miami) and blanks (Milli-Q water) were analyzed every five samples to check accuracy and baseline stability.
2.4 TG-corrected $p$CO$_2$

In situ $p$CO$_2$ often does not provide direct information about underlying biogeochemical processes, due to the fact that it is impacted strongly by temperature and moderately by air-sea gas exchange (as in shallow coastal water). Here we remove $p$CO$_2$ variations caused by the annual temperature cycle and air-sea gas exchange from the in situ $p$CO$_2$. The remaining $p$CO$_2$ is then assumed to be controlled primarily by biological activity and mixing. For simplicity, this temperature and air-sea gas exchange corrected $p$CO$_2$ will be called TG-corrected $p$CO$_2$ hereafter, and can be calculated as:

$$p$CO$_2$(TG-corrected) = p$CO$_2$(in situ) – [$\Delta p$CO$_2$(temp) + $\Delta p$CO$_2$(air-sea)] \quad (1)$$

in µ atm, where $p$CO$_2$(TG-corrected) is the temperature and air-sea gas exchange corrected sea surface $p$CO$_2$, $p$CO$_2$(in situ) is the observed sea surface $p$CO$_2$, $\Delta p$CO$_2$(temp) is the $p$CO$_2$ change caused by temperature deviation from the annual mean temperature, and $\Delta p$CO$_2$(air-sea) is the $p$CO$_2$ change due to air-sea gas exchange (also normalized to the annual mean sea surface temperature, SST).

Water temperature changes $p$CO$_2$ both by shifting the inorganic carbon equilibrium and by altering solubility. Assuming other parameters are constant, $p$CO$_2$ in water increases with increasing water temperature. The in situ $p$CO$_2$ can be normalized to a constant temperature using the equation of Takahashi et al. (1993, 2002):

$$p$CO$_2$(SST) = p$CO$_2$(in situ) × exp[0.0423 × (SST – SST)] \quad (2)$$

where SST is the annual mean SST, and $p$CO$_2$(SST) is the $p$CO$_2$ normalized to the annual mean SST. Once $p$CO$_2$(SST) is calculated, the $p$CO$_2$ change due to the temperature deviation from the annual mean SST is then calculated as:

$$\Delta p$CO$_2$(temp) = p$CO$_2$(in situ) – $p$CO$_2$(SST) \quad (3)$$

It should be noted that the $p$CO$_2$ change due to temperature deviation from the annual mean SST is relative to the annual mean temperature used for the calculation.
Because aqueous CO$_2$ dissociates in water, the $p$CO$_2$ change due to air-sea gas exchange cannot be estimated based on linear dilution of CO$_2$ itself. Instead, it is calculated from changes in DIC and alkalinity. First, carbonate alkalinity (CA) is calculated from $p$CO$_2$ and DIC at in situ temperature and salinity. Assuming the surface mixed layer in the SAB extends to the seafloor in all sampling months (as is the case for most of the cruises except July 2005), the DIC concentration prior to air-sea gas exchange (in mmol m$^{-3}$) can be calculated as:

$$\text{DIC}_{\text{prior}} = \frac{\text{DIC(per area)}_{\text{in situ}} - \Delta \text{DIC(air-sea)}}{\text{Depth}}$$

(4)

Here, DIC(per area)$_{\text{in situ}}$ is the integrated DIC in the water column (units of mmol m$^{-2}$), and $\Delta \text{DIC(air-sea)}$ is the amount of DIC gain or loss caused by air-sea gas exchange (units of mmol m$^{-2}$). Positive $\Delta \text{DIC(air-sea)}$ values indicate addition of CO$_2$ to seawater through air-sea gas exchange. As a first-order approximation, a 30-day (mean residence time of the entire SAB was 30–90 days, Atkinson et al., 1978; Moore, 2007) air-sea gas exchange time was used to calculate the $\Delta \text{DIC(air-sea)}$. Additional information about how air-sea CO$_2$ fluxes were calculated can be found in Jiang et al. (2008a).

Once DIC$_{\text{prior}}$ is calculated, $p$CO$_2$(SST)$_{\text{prior}}$ ($p$CO$_2$ before air-sea gas exchange at the annual mean temperature), can be calculated from DIC$_{\text{prior}}$ and CA at the annual mean temperature and the in situ salinity. Then, $\Delta p$CO$_2$(air-sea) can be calculated as the difference between $p$CO$_2$(SST) and $p$CO$_2$(SST)$_{\text{prior}}$.

After both $\Delta p$CO$_2$(temp) and $\Delta p$CO$_2$(air-sea) have been estimated, TG-corrected $p$CO$_2$ can be calculated from Eq. (1). As we can see, if $\Delta p$CO$_2$(temp) in Eq. (1) is substituted with the right-hand side of Eq. (3), the following is derived:

$$p\text{CO}_2(\text{TG-corrected}) = p\text{CO}_2(\text{SST}) - \Delta p\text{CO}_2(\text{air-sea})$$

(5)

Thus, in addition to the definition given in Eq. (1), $p$CO$_2$ (TG-corrected) may also be expressed as temperature-normalized $p$CO$_2$ corrected by the $p$CO$_2$ change due to air-sea gas exchange.
2.5 \textit{pCO}_2\textit{ from river, marsh, and within-shelf sources}

Contributions of \textit{pCO}_2 (TG-corrected) can be divided into three components: $\Delta \text{pCO}_2$ (river), the \textit{pCO}_2 change due to river inputs; $\Delta \text{pCO}_2$ (marsh), the \textit{pCO}_2 change due to salt marsh inputs; and $\Delta \text{pCO}_2$ (shelf), the \textit{pCO}_2 change due to biological activity and other processes on the shelf. Based on the conceptual diagram proposed in Fig. 2, $\Delta \text{pCO}_2$ (river), $\Delta \text{pCO}_2$ (marsh), and $\Delta \text{pCO}_2$ (shelf) can be calculated by the following equations (Fig. 2):

\begin{align*}
\Delta \text{pCO}_2 (\text{river}) &= \text{pCO}_2 R - \text{pCO}_2 \text{base} \\
\Delta \text{pCO}_2 (\text{marsh}) &= \text{pCO}_2 R + M - \text{pCO}_2 R \\
\Delta \text{pCO}_2 (\text{shelf}) &= \text{pCO}_2 (\text{TG-corrected}) - \text{pCO}_2 R + M
\end{align*}

where, \text{pCO}_2 (\text{base}) is the \textit{pCO}_2 if the oceanic end-member is only diluted by freshwater that contains no DIC, \text{pCO}_2 (\text{base}) can be calculated from its corresponding DIC$_{\text{base}}$ and TA$_{\text{base}}$ that were calculated based on linear mixing of the open ocean end-members with zero-DIC freshwater (Fig. 2). \text{pCO}_2 R is the \textit{pCO}_2 if the ocean end-member is only mixed with the river end-member. Similarly, \text{pCO}_2 R can be calculated from its corresponding DIC$_{R}$ and TA$_{R}$ derived from the ocean and river end-members (Fig. 2). \text{pCO}_2 R + M is the \textit{pCO}_2 if the ocean end-member is only mixed with the nearshore end-member which contains inputs from both the river and marsh. Again, \text{pCO}_2 R + M can be estimated from its corresponding DIC$_{R + M}$ and TA$_{R + M}$ using the same method (Fig. 2).

Table 1 shows the end-members used for the calculation. The river end-members were collected from the Altamaha River (JayCee Landing in Jesup, Georgia, 31°67' N, 81°85' W). Earlier studies have shown that the Altamaha River provides a good representation of the river end-members in the South Atlantic Bight (Cai and Wang 1998; Cai et al. 2010). The nearshore and open ocean end-members were chosen as the most nearshore and offshore stations of the central transect, respectively (Table 1).
The above method has been demonstrated to work well in estuaries (Jiang et al., 2008b). However, unlike estuaries, where mixing occurs between two end-members in a restricted physical environment, the mixing processes on the continental shelf are far more complicated (Menzel, 1993). Mixing here occurs in both cross-shelf and along-shelf directions, and is complicated by the existence of the Coastal Frontal Zone. These complex mixing processes make it challenging to choose which specific nearshore end-members to use. As a result, the selection of nearshore end-members could cause uncertainties in the estimated $\Delta pCO_2$ (marsh) and $\Delta pCO_2$ (shelf). In addition, the nearshore end-members are not temporally stable relative to the residence time of the shelf, because primary production and respiration in the nearshore areas are highest and show the largest seasonal variation of the entire shelf (Griffith et al., 1990; Verity et al., 1993; Cai, 2010). This again will bring about large uncertainties (Loder and Reichard, 1981). Nonetheless, we believe our approach represents a progress to solve this challenging issue to the coastal ocean carbon cycle community.

3 Results

3.1 Dissolved inorganic carbon

DIC concentrations in the SAB (within 100 m water depth) ranged from 1900 to 2100 µmol kg$^{-1}$ (Fig. 3). In all sampling months, DIC was lowest close to the coast and increased towards the shelf break. Nearshore DIC showed the largest seasonal variation, and was lowest in March and October 2005 when the shelf received the greatest amount of freshwater discharge. In comparison, DIC at the ocean end-member was relatively invariant with season. It is clear that the nearshore DIC concentrations were higher than predicted from the mixing line up to a salinity of 34 (Fig. 3).
3.2 Dissolved organic carbon

DOC concentrations in the SAB showed a negative correlation with salinity (Fig. 4), indicating input of organic carbon from terrestrial sources. Spatially, the highest DOC concentrations occurred in the middle of the proximal SAB (160–170 µmol l\(^{-1}\) in March 2005 and May 2006, and 230–240 µmol l\(^{-1}\) in July and October 2005). Surface water DOC beyond the CFZ was much lower at 70–100 µmol l\(^{-1}\). In July 2005 unusually high DOC concentrations were observed in the distal SAB (134 µmol l\(^{-1}\)) off South Carolina where low salinity waters were found (Fig. 4, Jiang et al., 2008a).

3.3 Impact of temperature on sea surface \(pCO_2\)

The annual temperature cycle resulted in lower \(pCO_2\) in winter and spring, and higher \(pCO_2\) in summer throughout the SAB shelf (Fig. 5). Area-averaged in situ \(pCO_2\) was under-saturated all across the shelf during winter and spring, and increased towards summer (Fig. 5). From May to October, the shelf became super-saturated with the inner shelf showing the highest \(pCO_2\). The magnitude of \(\Delta pCO_2(\text{temp})\) on the inner shelf was larger than that on the outer shelf, partly due to the greater seasonal range of SST on the proximal SAB shelf (10–30 °C) compared to the distal SAB shelf (20–30 °C) (Jiang et al., 2008a).

3.4 Impact of air-sea gas exchange on sea surface \(pCO_2\)

Air-sea gas exchange had the net effect of modulating the seasonal changes of \(pCO_2\) in the SAB. It increased \(pCO_2\) in winter when sea surface \(pCO_2\) was under-saturated and decreased it in summer when \(pCO_2\) was supersaturated (Fig. 5). However, while air-sea gas exchange played an important role in changing \(pCO_2\) on the proximal SAB shelf, greater water depths and consequently greater integrated DIC in the mixed layer on the distal SAB shelf make air-sea gas exchange insignificant in controlling the \(pCO_2\) there (Fig. 5).
3.5 TG-corrected $pCO_2$

During warm months (July and October 2005), when sea surface temperature (Fig. 4 in Jiang et al. 2008a) was homogeneous all over the continental shelf, surface water TG-corrected $pCO_2$ (Fig. 6) showed similar spatial distribution as in situ $pCO_2$ (Fig. 4 in Jiang et al. 2008a). They were both highest close the coast and decreased with distance offshore. During cold months (January, March, and December 2005), while TG-corrected $pCO_2$ was still higher close to the coast than offshore, the trend was reversed for the in situ $pCO_2$ (Fig. 4 in Jiang et al., 2008a). The contrasting spatial variations in winter were due to the large onshore-offshore temperature gradients at this time of the year (SST in winter was about 10–14 °C close to the coast and increased to 20–25 °C at the shelf break, Jiang et al., 2008a).

The area-averaged TG-corrected $pCO_2$ on the middle and outer shelf showed similar seasonal variation, i.e., increasing from January to March, leveling off in May, decreasing in July and October, and then increasing again in December (Fig. 5). On the inner shelf, the area-averaged TG-corrected $pCO_2$ was lowest in January, and showed the largest increase in March and October (Fig. 5) when the shelf experienced the greatest river discharges.

3.6 $\Delta pCO_2$(river), $\Delta pCO_2$(marsh), and $\Delta pCO_2$(shelf)

Contributions of CO$_2$ from the river [$\Delta pCO_2$(river)] were highest close to the coast and decreased with distance offshore (Fig. 7). During January and March 2005, $\Delta pCO_2$(river) was up to 30 µatm on the inner shelf but averaged only 0–3 µatm on the outer shelf. Seasonally, $\Delta pCO_2$(river) was highest in January, March, and October 2005 (Fig. 8). Contributions of CO$_2$ from salt marshes [$\Delta pCO_2$(marsh)] showed similar spatial and seasonal distributions as $\Delta pCO_2$(river), with the magnitude of $\Delta pCO_2$(marsh) being about three times as high as that of $\Delta pCO_2$(river) (Figs. 8 and 9). Contributions of CO$_2$ from within the shelf [$\Delta pCO_2$(shelf)] were highest of the three components (Figs. 8 and 10). Compared to $\Delta pCO_2$(river) and
$\Delta pCO_2$(marsh), $\Delta pCO_2$(shelf) showed much smaller onshore-offshore gradients in January and March 2005. Seasonally, $\Delta pCO_2$(shelf) was highest in May 2006 and October 2005.

4 Discussion

4.1 Carbon input from terrestrial sources

In addition to nutrients, continental shelves receive large amounts of organic and inorganic carbon from terrestrial sources. In the following discussion, “terrestrial” refers to all influences landward the land-ocean boundary, including rivers, estuaries, salt marshes, groundwater, and other land-derived sources. The input of organic carbon can be readily seen from the seaward decrease of DOC concentrations (Fig. 4). In contrast to DOC, the DIC transport on the shelf is less obvious. DIC on the continental shelf contains a large oceanic component that could easily mask the DIC signals from land. Therefore, the seaward increase of DIC concentrations does not necessarily mean that the shelf is transporting DIC landward (Fig. 3). To examine the DIC inputs from terrestrial sources (as well as net ecosystem metabolism, or NEM), total excess DIC ($DIC_{T-excess}$) was calculated according to Jiang et al. (2008b):

$$DIC_{T-excess} = DIC_i - \frac{S_i}{S_{ocean}} \times DIC_{ocean}$$

(9)

in $\mu$mol kg$^{-1}$, where $DIC_i$ and $DIC_{ocean}$ are DIC concentrations of station $i$ and the ocean end-member, respectively, and $S_i$ and $S_{ocean}$ are salinities of station $i$ and the ocean end-member, respectively. The second term on the right-hand side of Eq. (9) ($\frac{S_i}{S_{ocean}} \times DIC_{ocean}$) represents the oceanic DIC component (that is $DIC_{base}$ in Fig. 2a). Total excess DIC defined here represents all DIC sources or sinks (e.g., all terrestrial inputs as well as NEM on the shelf) except those from the open ocean.
The calculated total excess DIC was highest on the central part of the inner shelf (140–180 µmol l\(^{-1}\)) and lowest on the outer shelf (−10 to 50 µmol l\(^{-1}\)) (Fig. 11). Like DOC, the total excess DIC shows negative correlation with salinity in all sampling months, suggesting input of DIC from terrestrial sources (Fig. 11). Similarly, excess DOC was also calculated. Not surprisingly, excess DOC was also highest close to the coast and decrease with distance offshore (Fig. 12).

4.2 Impact of terrestrial carbon on continental shelf CO\(_2\)

Even though the contribution of DIC from terrestrial sources is usually much smaller when compared to that from the open ocean, a much larger proportion of the terrestrial DIC exists in the form of aqueous CO\(_2\). As a result, terrestrial DIC input plays a critical role in elevating CO\(_2\) concentrations in continental shelf waters. Terrestrial sources increase the nearshore \(p\text{CO}_2\) directly through input of inorganic carbon from rivers (Cai and Wang, 1998; Cai et al., 1999; Jiang et al., 2008b) and salt marshes (Wang and Cai, 2004), and indirectly by input of organic carbon (Moran et al., 1991; Alberts and Takács, 1999; DeAlteris, 2007) that is later remineralized partially on the shelf.

Rivers discharging to the SAB enhance \(p\text{CO}_2\) on the continental shelf by delivering water with high CO\(_2\) concentrations that arise ultimately from microbial decomposition of organic matter in soils, river waters, and sediments (Jones and Mulholland, 1998; Neal et al., 1998; Cole and Caraco, 2001). Studies of the Altamaha and Satilla River estuaries have shown that rivers discharging to the SAB are highly supersaturated with respect to atmospheric CO\(_2\). During summer, surface water \(p\text{CO}_2\) in these river-dominated estuaries is as high as \(\sim 4000 \mu\text{atm}\) compared to only about \(\sim 400–600 \mu\text{atm}\) on the continental shelf (Cai and Wang, 1998; Jiang et al., 2008b).

Salt marshes contribute to \(p\text{CO}_2\) in the SAB by direct release of inorganic carbon to the shelf. An important feature of this region is the extensive areas of inter-tidal salt marshes (Pomeroy and Wiegert, 1981). The dominant primary producer in these marshes is \textit{Spartina alterniflora}, which has among the highest primary productivity of any ecosystem (\(\sim 1100\) to 2250 gC m\(^{-2}\) yr\(^{-1}\), Dai and Wiegert, 1996). CO\(_2\) that is
released to intertidal marsh sediments and waters by bacterial remineralization of *Spartina*-derived organic matter can be exported to coastal waters (Cai et al., 1999; Wang and Cai, 2004; Jiang et al., 2008b) via tidal flushing (Neubauer and Anderson, 2003) and drainage of sediment interstitial waters (Jahnke et al., 2003).

Rivers and salt marshes also transport significant amounts of organic carbon to the SAB (Fig. 12), the remineralization of which by microbes (Pomeroy et al., 2000; Jahnke et al., 2005) and photochemistry (Miller and Moran, 1997) in shelf waters and sediments will further increase the nearshore $p\text{CO}_2$. Earlier studies have shown that most nutrients entering the SAB occur in organic form that must be remineralized before they may be taken up by phytoplankton (Dunstan and Atkinson, 1976; Hanson et al., 1990; DeAlteris, 2007). The potential importance of this pathway in enhancing $p\text{CO}_2$ on the proximal SAB is supported by the positive correlation between TG-corrected $p\text{CO}_2$ and excess DOC (figure not shown).

### 4.3 Seasonal changes of $\text{CO}_2$ inputs to the proximal SAB

Seasonally, $\text{CO}_2$ from the SAB rivers and salt marshes is largely related to river discharge rates, and greater amounts of $\text{CO}_2$ will be transported to the shelf at higher discharge rates (Borges et al. 2006; Jiang et al., 2008b). This can be seen from the high $\Delta p\text{CO}_2$(river) and $\Delta p\text{CO}_2$(marsh) during January and March 2005 (high flow seasons, Jiang, 2009) than in May 2006 and July 2005 (low flow seasons) (Fig. 8).

The $\text{CO}_2$ production from within the shelf (e.g. NEM), on the other hand, is predicted to be strongly dependent on temporal changes in organic matter remineralization and shelf water residence time. Respiration rates in the proximal SAB have been shown to be nearly an order of magnitude higher in summer and fall than in winter and spring (Hopkinson, 1985; Griffith et al., 1990; Jiang et al., 2010). However, the additional $\text{CO}_2$ released from heterotrophic processes in summer may be counterbalanced by greater $\text{CO}_2$ uptake due to aquatic primary production at this time of the year (Verity et al., 2002). The results of $\Delta p\text{CO}_2$(shelf) suggest that the shelf is more likely to be heterotrophic (releasing $\text{CO}_2$) during summer and fall (May 2006, July and October
2005), and relatively more autotrophic during winter and spring (January and March 2005) (Fig. 8). This is confirmed by the δ¹³ values of DIC in the proximal SAB, which became significantly more depleted as the seasons progress from spring to fall (DeAlteris, 2007). The relatively lower CO₂ production during July 2005 might be related to a Gulf Stream intrusion, which increased biological production and counter-balance the DIC production.

5 Conclusions

Analyses of the DIC, DOC, and pCO₂ data in the SAB demonstrate how temperature, air-sea gas exchange, and terrestrial inputs control sea surface pCO₂ on the continental shelf. Terrestrial sources increase the nearshore pCO₂ by direct input of inorganic carbon from rivers and salt marshes, and indirectly by input of organic carbon that is later remineralized in the SAB. This mechanism is the most likely explanation for findings of the proximal SAB (inner shelf) being a source of atmospheric CO₂ (+1.2 mol m⁻² yr⁻¹), and the distal SAB (middle and outer shelf) being a sink of −1.3 mol m⁻² yr⁻¹ (Jiang et al., 2008a).

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References


Jiang, L. Q.: Biogeochemical cycling of carbon dioxide in estuaries and the continental shelf of the Southeastern United States, Ph.D., Marine Science, University of Georgia, Athens, 172 pp., 2009.


Table 1. River, nearshore and open ocean end-members used for the calculation. DIC and TA stand for dissolved inorganic carbon and total alkalinity, respectively. The units are μmol kg$^{-1}$.

<table>
<thead>
<tr>
<th>Month</th>
<th>River end-member</th>
<th>Nearshore end-member</th>
<th>Open ocean end-member</th>
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<tbody>
<tr>
<td></td>
<td>Salinity</td>
<td>DIC</td>
<td>TA</td>
</tr>
<tr>
<td>Jan 2005</td>
<td>0.0</td>
<td>560.0</td>
<td>479.3</td>
</tr>
<tr>
<td>Mar 2005</td>
<td>0.0</td>
<td>498.0</td>
<td>473.1</td>
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<tr>
<td>May 2006</td>
<td>0.0</td>
<td>727.6</td>
<td>753.2</td>
</tr>
<tr>
<td>Jul 2005</td>
<td>0.0</td>
<td>527.2</td>
<td>414.3</td>
</tr>
<tr>
<td>Oct 2005</td>
<td>0.0</td>
<td>894.9</td>
<td>842.0</td>
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</table>
**Fig. 1.** Study area in the US South Atlantic Bight between Cape Lookout, North Carolina to Cape Canaveral, Florida. Open circles are the sampling stations, which start from the shoreline and extend to about ~500 m water depth.
Fig. 2. Conceptual diagrams showing DIC and dissolved CO$_2$ concentrations during continental shelf mixing. (a) shows DIC concentrations against salinity. On the X-axis, $S_i$ and $S_{ocean}$ are salinity of station $i$ and the ocean end-member, respectively. On the Y-axis, DIC$_{ocean}$, DIC$_{river+marsh}$ and DIC$_{river}$ are DIC of the ocean end-member, nearshore end-member (containing DIC from both the river and marsh), and the river end-member, respectively. On the right side, DIC$_i$ is the in situ DIC, and DIC$_{R+M}$, DIC$_{R}$, and DIC$_{base}$ are the DIC at the salinity of $S_i$ if the ocean end-member is mixed only with the nearshore end-member (containing DIC from both the river and marsh), the river end-member, and zero-DIC freshwater end-member, respectively. (b) shows dissolved CO$_2$ concentrations against salinity. Their corresponding $p$CO$_2$ can be calculated according to $p$CO$_2$ = $k_H$ \cdot (CO$_2$), where $k_H$ is Henry constant.
Fig. 3. Plots of dissolved inorganic carbon (DIC) for depths shallower than 100 m plotted against salinity in all sampling months. The dotted lines connect the river and ocean end-members.
Fig. 4. Surface water dissolved organic carbon (DOC) plotted against salinity in March, July, and October 2005 in the South Atlantic Bight.
**Fig. 5.** Seasonal changes of area-averaged sea surface $pCO_2$, $pCO_2$ variations due to temperature deviation from the annual mean temperature (23.11 °C), $pCO_2$ variations due to air-sea gas exchange, and TG-corrected $pCO_2$ on the SAB. In situ $pCO_2$ equals the sum of $pCO_2$ variations due to temperature, $pCO_2$ variations due to air-sea gas exchange, and TG-corrected $pCO_2$ (Eq. 1).
Fig. 6. Spatial distributions of surface water TG-corrected $pCO_2$ on the South Atlantic Bight in all sampling months except December 2005. Due to lack of DIC data, spatial distribution of TG-corrected $pCO_2$ in December 2005 was not presented. The colored contours are from triangle-based liner interpolation.
Fig. 7. Spatial distributions of $\Delta pCO_2$ (river) or the portion of sea surface $pCO_2$ that is due to inputs from the river (normalized to 23.11 °C). Due to lack of DIC data, $\Delta pCO_2$ (river) in December 2005 was not presented. The colored contours are from triangle-based linear interpolation.
Fig. 8. Seasonal changes of area-averaged $\Delta p\text{CO}_2$ (river) or sea surface $p\text{CO}_2$ that is due to inputs from the river (normalized to 23.11 °C), $\Delta p\text{CO}_2$ (marsh) or sea surface $p\text{CO}_2$ that is due to inputs from the marsh, and $\Delta p\text{CO}_2$ (shelf) or sea surface $p\text{CO}_2$ that is due to processes on the shelf.
Fig. 9. Spatial distributions of $\Delta p\text{CO}_2$ (marsh) or the portion of sea surface $p\text{CO}_2$ that is due to inputs from the marsh (normalized to 23.11°C). Due to lack of DIC data, $\Delta p\text{CO}_2$ (marsh) in December 2005 was not presented. The colored contours are from triangle-based linear interpolation.
Fig. 10. Spatial distributions of $\Delta p$CO$_2$ (shelf) or the portion of sea surface $p$CO$_2$ that is due to inputs from the shelf (normalized to 23.11°C). Due to lack of DIC data, $\Delta p$CO$_2$ (shelf) in December 2005 was not presented. The colored contours are from triangle-based linear interpolation.
**Fig. 11.** Surface water total excess DIC plotted against salinity in January, March, July, October 2005 and May 2006 in the South Atlantic Bight. Due to lack of data, total excess DIC in December 2005 was not calculated.
Fig. 12. Surface water excess DOC plotted against salinity in March, July, October 2005 and May 2006 in the South Atlantic Bight. Due to lack of data, excess DOC in January and December 2005 was not calculated.