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Influence of terrestrial inputs on continental shelf carbon dioxide

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Abstract. The US South Atlantic Bight (SAB) is a low-latitude shallow continental shelf bordered landward by abundant salt marshes and rivers. Based on previously published data on sea surface partial pressure of carbon dioxide (pCO_2) and new dissolved inorganic carbon (DIC) and dissolved organic carbon (DOC) data, a model analysis is presented to identify and quantify the contributions of various terrestrial carbon inputs on SAB sea surface pCO_2. After removal of pCO_2 variations due to annual temperature variability and air–sea gas exchange from the in situ pCO_2, the temperature- and gas-exchange-corrected pCO_2 (TG-corrected pCO_2) is derived. Contributions from rivers, salt marshes, and the continental shelf to the TG-corrected pCO_2 are then calculated. Our findings demonstrate that although additions of CO_2 from within shelf waters (i.e., $\Delta pCO_2(\text{shelf})$) were the greatest of the three components and underwent the largest seasonal changes, $\Delta pCO_2(\text{shelf})$ showed smaller onshore–offshore gradients than rivers and marshes. In contrast, CO_2 contributions from river ($\Delta pCO_2(\text{river})$) and salt marsh ($\Delta pCO_2(\text{marsh})$) components were greatest closest to the coast and decreased with distance offshore. In addition, the magnitude of $\Delta pCO_2(\text{marsh})$ was about three-fold greater than $\Delta pCO_2(\text{river})$. Our findings also revealed that decomposition of terrestrial organic carbon was an important factor regulating the seasonal pattern of pCO_2 on the inner shelf. Despite large uncertainties, this study demonstrates the importance of terrestrial inputs, in particular those from coastal wetlands, on coastal ocean CO_2 distributions.

1 Introduction

Continental shelves play a key role in the global carbon cycle by linking terrestrial, marine and atmospheric systems (Mackenzie, 1991; Smith and Hollibaugh, 1993). Despite their relatively small size (~ 7–8% of the global ocean surface area), continental shelves sustain disproportionately high rates of primary production, remineralization, and organic carbon burial (Walsh, 1988; Wollast, 1993; Gattuso et al., 1998; de Hass et al., 2002). Recent studies have further shown that continental shelves are a globally important sink of atmospheric carbon dioxide (CO_2) (Borges et al., 2005; Cai et al., 2006; Chen and Borges, 2009).

The majority of continental shelves, in particular those that are both wide and aligned with a western boundary current, can be divided into two zones: the proximal (i.e., inner) shelf that is strongly impacted by land, and the distal (i.e., middle and outer) shelf that is influenced to a greater extent by open ocean waters (Rabouille et al., 2001). Relative to the distal shelf, the proximal shelf generally shows much steeper biogeochemical gradients owing to its proximity to inputs from land, including rivers, estuaries and salt marshes. Therefore, higher resolution surveys are warranted to understand the biogeochemical processes on the proximal shelf, although it has often been neglected in continental shelf CO_2 studies.

Continental shelves are strongly impacted by inputs of nutrients and organic and inorganic carbon from land (Thomas et al., 2004). As a result of nutrient inputs, proximal continental shelves typically 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 (Bauer and Bianchi, 2011; Bianchi and Bauer, 2011). In addition, direct inorganic carbon input from river waters plays an important role in enhancing pCO$_2$ 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 pCO$_2$ in continental shelf waters. Understanding the roles of these different processes in driving carbon and CO_2 exchanges in shelf waters is critical for establishing both the relative contributions of each to coastal carbon budgets and for predicting future changes due to changes in climate, hydrology and coastal circulation.

In order to differentiate the various components contributing to shelf carbon and CO_2 sources and fluxes, we investigated the South Atlantic Bight (SAB) off the southeastern United States. The SAB is a low-latitude shallow continental shelf bordered landward by abundant salt marshes and river discharge and seaward by a major western boundary current, the Gulf Stream. This unique geographical location offers well-defined and distinct landward and seaward components. A recent study has shown that while the distal SAB shelf is an atmospheric CO_2 sink of $-1.3\,\mathrm{mol\,m^{-2}\,yr^{-1}}$, the proximal SAB shelf is a source of $1.2\,\mathrm{mol\,m^{-2}\,yr^{-1}}$ (Jiang et al., 2008a). The goal of this study is to differentiate and quantify the contributions of the annual temperature cycle, air–sea gas exchange, and inputs from rivers, salt marshes and within shelf waters to sea surface pCO$_2$ in this region. Evaluating the roles of these different drivers will contribute to the understanding of carbon dioxide dynamics in the coastal ocean. The present study is based on CO_2 data previously reported in Jiang et al. (2008a), and new dissolved inorganic carbon (DIC) and dissolved organic carbon (DOC) data from the same cruises.

2 Study site and methods

2.1 Site description

The SAB continental shelf has an average depth of only 30 m and is 50–75 m deep at the shelf break (Menzel, 1993). The Gulf Stream flows northward along the shelf break (Fig. 1). The shorelines of Georgia and South Carolina are characterized by extensive salt marshes ($3000\,\mathrm{km^2}$, 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 $66\,\mathrm{km^3}$ ($\sim 2.7\,\%$ 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).
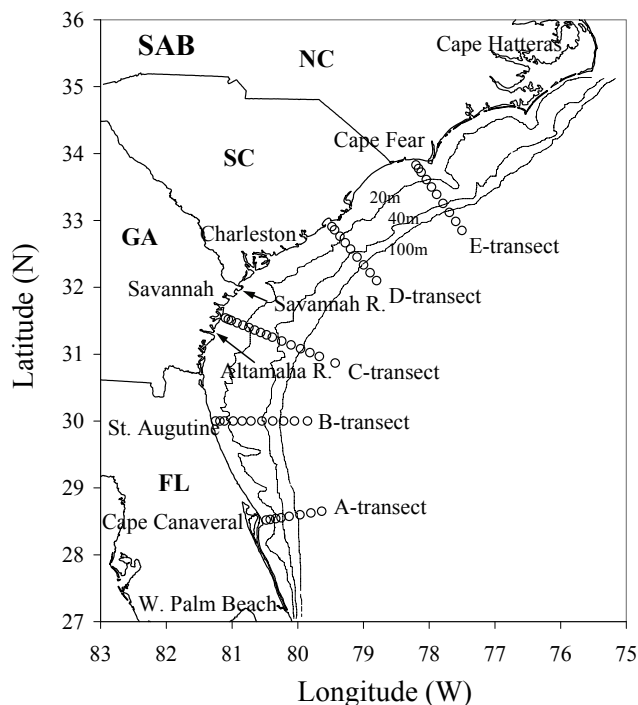
Fig. 1. Study area in the US South Atlantic Bight between Cape Lookout, North Carolina, and Cape Canaveral, Florida. Open circles indicate sampling stations, between the shoreline and extending to $\sim 500\,\mathrm{m}$ water depth.

A coastal frontal zone (CFZ), formed by a pressure gradient induced by freshwater discharge, frequently occurs at 10–30 m isobaths, about 10–30 km offshore on the SAB shelf (Blanton, 1981). For simplicity, we refer to the shelf shoreward the CFZ as the proximal SAB (roughly equivalent to the inner shelf, as defined in Jiang et al., 2008a), and the shelf seaward the CFZ as the distal SAB (roughly equivalent to the middle and outer shelf).

The proximal SAB (inner shelf) 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 (middle and outer 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: 5–16 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; Huang et al., 2012). DOC samples collected during the cruises of March, July, and October 2005 were measured in the Radiocarbon Laboratory of the Virginia Institute of Marine Science (VIMS) using a Shimadzu TOC-5000A high-temperature Pt-catalyzed analyzer with a mean analytical error of 1.4 μmol 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 and agreed within measurement error in both labs.

2.4 Calculation of temperature- and gas-exchange-corrected pCO$_2$

In situ pCO$_2$ often does not provide direct information about underlying biogeochemical processes, due to the fact that it is strongly impacted by temperature and air–sea gas exchange, as shown by Jiang et al. (2008a) in shallow coastal waters of SAB. Here we remove pCO$_2$ variations caused by the annual temperature cycle and air–sea gas exchange from the in situ pCO$_2$. The remaining pCO$_2$ is then assumed to be controlled primarily by biological activity and mixing. For simplicity, this temperature- and gas-exchange-corrected pCO$_2$ will be called TG-corrected pCO$_2$ hereafter, and can be calculated as

$$p\text{CO}_2(\text{TG-corrected}) = p\text{CO}_2(\text{in situ}) - [\Delta p\text{CO}_2(\text{temp})$$
$$+ \Delta p\text{CO}_2(\text{air-sea})], \tag{1}$$

where pCO$_2$ (TG-corrected) is the temperature- and gas-exchange-corrected sea surface pCO$_2$ (in μatm), pCO$_2$ (in situ) is the observed sea surface pCO$_2$, ΔpCO$_2$(temp) is the pCO$_2$ change caused by temperature deviation from the annual mean temperature, and ΔpCO$_2$(air-sea) is the pCO$_2$ change due to air–sea gas exchange (also referenced to the annual mean sea surface temperature, SST).

Water temperature changes pCO$_2$ both by shifting the inorganic carbon equilibrium and by altering solubility. As-

suming other parameters are constant, pCO$_2$ in water increases with increasing water temperature. The in situ pCO$_2$ can be referenced to a constant temperature using the equation of Takahashi et al. (1993, 2002):

$$p\text{CO}_2(\overline{\text{SST}}) = p\text{CO}_2(\text{in situ}) \times \exp[0.0423 \times (\overline{\text{SST}} - \text{SST})], \tag{2}$$

where $\overline{\text{SST}}$ is the annual mean SST, and pCO$_2$($\overline{\text{SST}}$) is the pCO$_2$ referenced to the annual mean SST. Once pCO$_2$($\overline{\text{SST}}$) is calculated, the pCO$_2$ change due to the temperature deviation from the annual mean SST is then calculated as

$$\Delta p\text{CO}_2(\text{temp}) = p\text{CO}_2(\text{in situ}) - p\text{CO}_2(\overline{\text{SST}}). \tag{3}$$

It should be noted that the pCO$_2$ change due to temperature deviation from the annual mean SST is relative to the temperature used for the calculation.

Because aqueous CO$_2$ dissociates in water, the pCO$_2$ 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 (Riebesell et al., 2010). To that end, first, carbonate alkalinity (CA) is calculated from pCO$_2$ and DIC at in situ temperature and salinity and then is held constant during the gas exchange process. 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

$$\text{DIC}_{\text{prior}} = \frac{\text{DIC}(\text{per area})_{\text{in situ}} - \Delta\text{DIC}(\text{air-sea})}{\text{Depth}}. \tag{4}$$

Here, DIC(per area)$_{\text{in situ}}$ is the integrated DIC in the water column, and ΔDIC(air-sea) is the amount of DIC gain or loss caused by air–sea gas exchange (both in mmol m^{-2}). Positive ΔDIC(air-sea) values indicate addition of CO$_2$ to seawater through air–sea gas exchange. As a first-order approximation, a 30-day air–sea gas exchange time was used to calculate the ΔDIC(air-sea), as mean residence time of the entire SAB is 30–90 days (Atkinson et al., 1978; Moore, 2007). 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, pCO$_2$($\overline{\text{SST}}$)$_{\text{prior}}$ (pCO$_2$ 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. ΔpCO$_2$(air-sea) can then be calculated as the difference between pCO$_2$($\overline{\text{SST}}$) and pCO$_2$($\overline{\text{SST}}$)$_{\text{prior}}$.

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

$$p\text{CO}_2(\text{TG-corrected}) = p\text{CO}_2(\overline{\text{SST}}) - \Delta p\text{CO}_2(\text{air-sea}). \tag{5}$$

Thus, in addition to the definition given in Eq. (1), pCO$_2$ (TG-corrected) may also be expressed as temperature-referenced pCO$_2$ corrected by the pCO$_2$ change due to air–sea gas exchange.

2.5 pCO$_2$ from river, marsh, and within-shelf sources

Contributions of pCO$_2$ (TG-corrected) can be divided into three components: ΔpCO$_2$(river), the pCO$_2$ change due to river inputs; ΔpCO$_2$(marsh), the pCO$_2$ change due to salt marsh inputs; and ΔpCO$_2$(shelf), the pCO$_2$ change due to biological activity and other processes on the shelf. ΔpCO$_2$(river), ΔpCO$_2$(marsh), and ΔpCO$_2$(shelf) can be calculated by the following equations (Fig. 2):

$$\Delta p\text{CO}_2(\text{river}) = p\text{CO}_{2_R} - p\text{CO}_{2_{\text{base}}} \tag{6}$$

$$\Delta p\text{CO}_2(\text{marsh}) = p\text{CO}_{2_{R+M}} - p\text{CO}_{2_R} \tag{7}$$

$$\Delta p\text{CO}_2(\text{shelf}) = p\text{CO}_2(\text{TG-corrected}) - p\text{CO}_{2_{R+M}}, \tag{8}$$

where pCO$_2$(base) is the pCO$_2$ if the oceanic end-member is only diluted by freshwater that contains no DIC. pCO$_2$(base) can be calculated from its corresponding DIC$_{\text{base}}$ and TA$_{\text{base}}$ that are calculated based on linear mixing of the open ocean end-members with the zero DIC and TA freshwater end-members (Fig. 2). pCO$_{2_R}$ is the pCO$_2$ if the ocean end-member is only mixed with the river end-member. Similarly, pCO$_{2_R}$ can be calculated from its corresponding DIC$_R$ and TA$_R$ (Fig. 2). pCO$_{2_{R+M}}$ is the 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, 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 Altamaha River (JayCee Landing in Jesup, Georgia, 31°67′ N, 81°85′ W). Earlier studies have shown that 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 area, 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 ΔpCO$_2$(marsh)
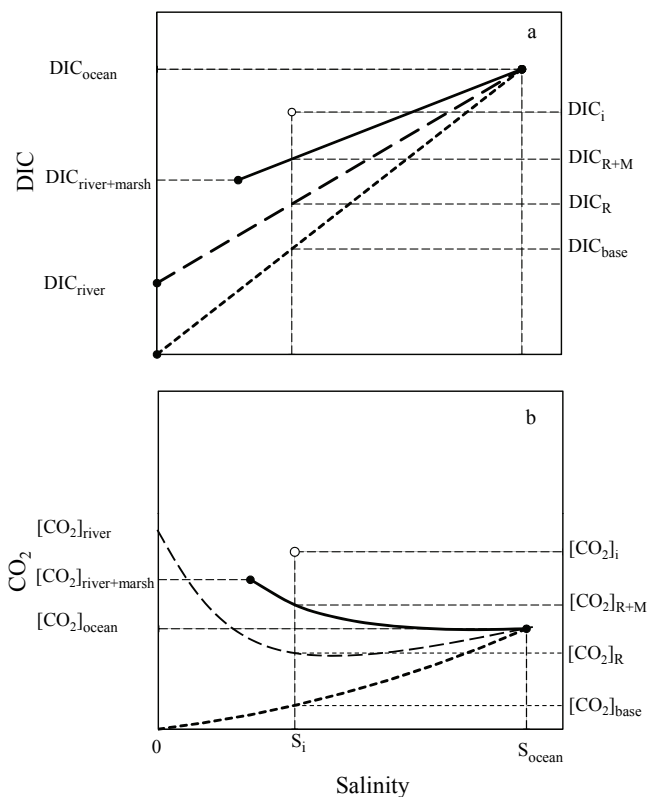

Fig. 2. Conceptual diagrams showing DIC and dissolved CO$_2$ concentrations during continental shelf mixing. **(a)** DIC concentration vs. salinity. On the x-axis, S_i and S_{ocean} are the salinities of station i and the ocean end-member, respectively. On the y-axis, DIC$_{\text{ocean}}$, DIC$_{\text{river+marsh}}$ and DIC$_{\text{river}}$ are DIC concentrations of the oceanic 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 concentration, and DIC$_{R+M}$, DIC$_R$, and DIC$_{\text{base}}$ are the DIC concentrations at the salinity of S_i assuming 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)** Dissolved CO$_2$ concentrations vs. salinity. The corresponding pCO$_2$ can be calculated according to pCO$_2 = k_H \cdot (\text{CO}_2)$, where k_H is Henry's constant.

and ΔpCO$_2$(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, unpublished data). This again will bring about large uncertainties (Loder and Reichard, 1981).

Table 1. River, nearshore and open ocean end-members used in calculations described in Sect. 2.5. DIC and TA designate dissolved inorganic carbon and total alkalinity, respectively, with nits of μmol kg^{-1}.

| Month	River end-member			Nearshore end-member			Open ocean end-member		
	Salinity	DIC	TA	Salinity	DIC	TA	Salinity	DIC	TA
Jan 2005	0.0	560.0	479.3	31.8	1943.2	2194.1	36.5	2040.0	2414.2
Mar 2005	0.0	498.0	473.1	30.7	1896.3	2104.4	36.3	2077.3	2407.5
May 2006	0.0	727.6	753.2	33.2	2019.8	2356.4	36.5	2070.3	2495.3
Jul 2005	0.0	527.2	414.3	31.2	1994.6	2235.0	35.9	2016.5	2393.8
Oct 2005	0.0	894.9	842.0	28.7	1908.9	2103.1	36.0	1985.4	2398.0
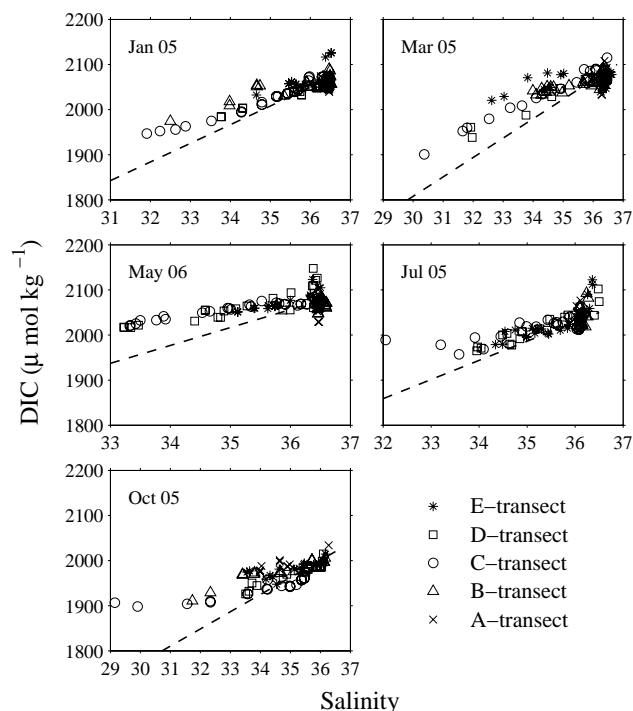
Fig. 3. Dissolved inorganic carbon (DIC) concentrations at depths shallower than 100 m vs. salinity and grouped by sampling month. The dotted lines connect the river and ocean end-members.

3 Results

3.1 Dissolved inorganic carbon

DIC concentrations in the SAB (i.e., < 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. The nearshore DIC concentrations were higher than predicted from the conservative mixing line up to a salinity of 34 (Fig. 3).
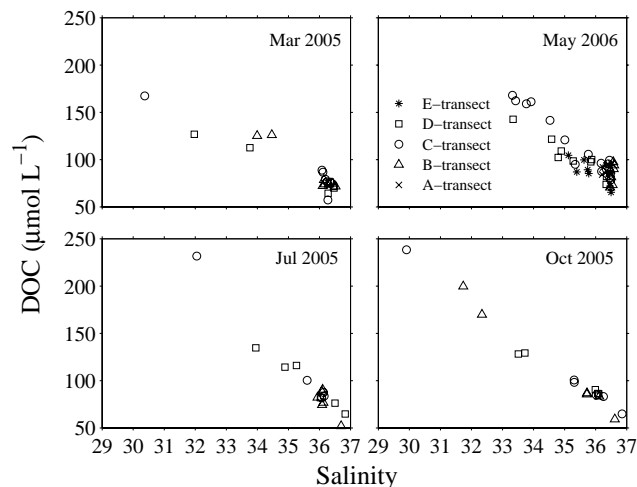

Fig. 4. Surface water dissolved organic carbon (DOC) vs. salinity in March, July, and October 2005 in the South Atlantic Bight.

3.2 Dissolved organic carbon

DOC concentrations in the SAB were negatively correlated with salinity (Fig. 4), indicating inputs of organic carbon from low salinity rivers and terrestrial sources. Spatially, the highest DOC concentrations occurred in the center (alongshore) of the inner shelf (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 outer SAB (134 μmol L^{-1}) off South Carolina where low salinity waters were observed (see Fig. 3, Jiang et al., 2008a).

3.3 Impact of temperature on sea surface pCO$_2$

The annual temperature cycle throughout the SAB shelf resulted in lower pCO$_2$ in winter and spring, and higher pCO$_2$ in summer (Fig. 5). Area-averaged in situ pCO$_2$ was undersaturated across the entire shelf during winter and spring, and increased into the summer months (Fig. 5). From May to October the shelf became super-saturated, with the inner shelf showing the highest pCO$_2$. The magnitude of ΔpCO$_2$(temp)
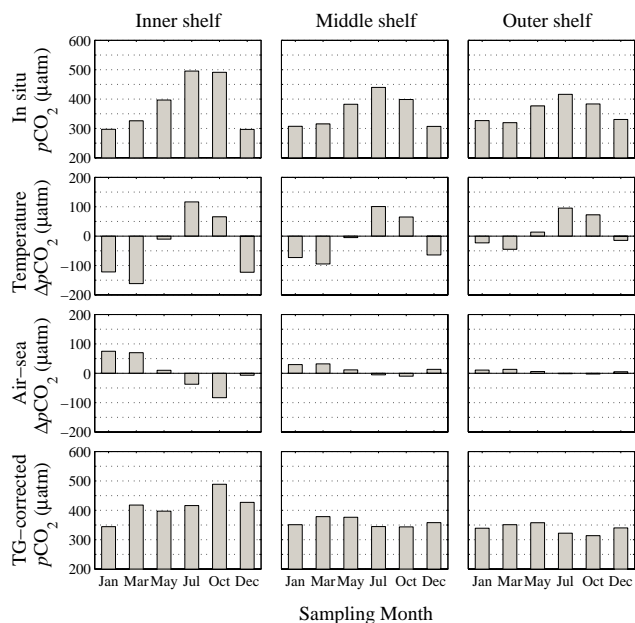
Fig. 5. Seasonal changes of area-averaged sea surface pCO$_2$, pCO$_2$ variations due to temperature deviation from the annual mean temperature (23.11 °C), pCO$_2$ variations due to air–sea gas exchange, and TG-corrected pCO$_2$ on the SAB. In situ pCO$_2$ is the sum of pCO$_2$ variations due to temperature, pCO$_2$ variations due to air–sea gas exchange, and TG-corrected pCO$_2$ (see Eq. 1 in text).

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 with 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 inner shelf, greater water depths and consequently greater integrated DIC inventory in the mixed layer on the outer shelf made 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 (see Fig. 2 in Jiang et al., 2008a) was homogeneous over the entire SAB continental shelf, surface water TG-corrected pCO$_2$ (Fig. 6) showed similar spatial distributions as in situ pCO$_2$ (see Fig. 4 in Jiang et al., 2008a). Both were highest close to the coast and decreased with distance offshore. During winter (January, March, and December 2005), while TG-corrected pCO$_2$ was still higher close
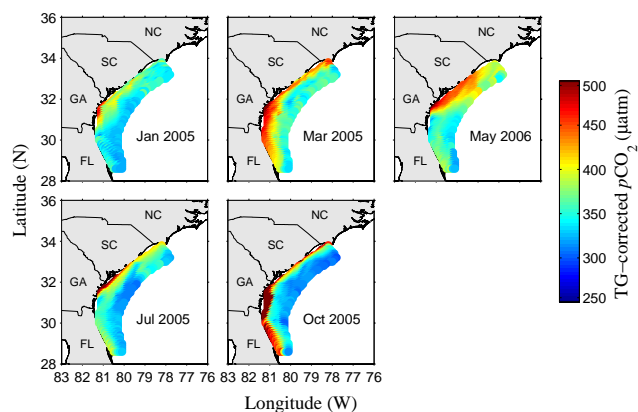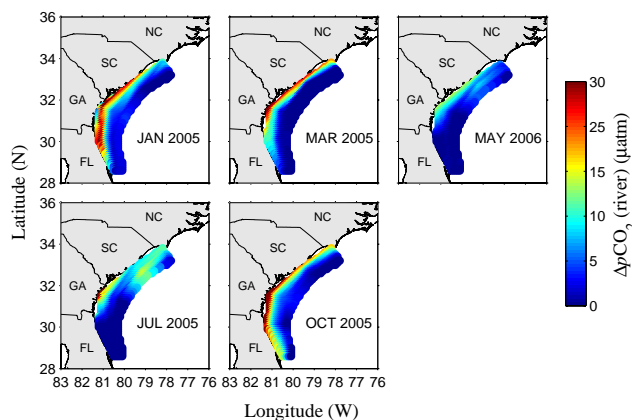

Fig. 6. Spatial distributions of surface water TG-corrected pCO$_2$ in the South Atlantic Bight in all sampling months except December 2005. Due to a lack of DIC data, spatial distribution of TG-corrected pCO$_2$ in December 2005 is not presented. The colored contours are from triangle-based liner interpolation.

to the coast than offshore, the trend was reversed for the in situ pCO$_2$ (see 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 ∼ 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 ΔpCO$_2$(river), ΔpCO$_2$(marsh), and ΔpCO$_2$(shelf)

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

Fig. 7. Spatial distributions of ΔpCO$_2$(river), or the portion of sea surface pCO$_2$ that is due to inputs from the river (referenced to 23.11 °C). Due to a lack of DIC data, ΔpCO$_2$(river) in December 2005 is not presented. The colored contours are from triangle-based liner interpolation.

4 Discussion

4.1 Carbon inputs 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 sources landward of the land/ocean boundary, including rivers, estuaries, salt marshes, groundwater, and other land-derived sources. Inputs of organic carbon can be readily seen from the seaward decreases of DOC concentrations (Fig. 4). In contrast to DOC, DIC transport on the shelf is less obvious. DIC on the continental shelf contains a large oceanic component that may mask the DIC signal from terrestrial sources. Therefore, seaward increases in DIC concentrations do not necessarily indicate 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$_{T\text{-excess}}$) was calculated according to Jiang et al. (2008b):

$$\text{DIC}_{\text{T-excess}} = \text{DIC}_i - \frac{S_i}{S_{\text{ocean}}} \times \text{DIC}_{\text{ocean}} \qquad (9)$$

in µmol kg^{-1} or mmol m^{-3}, where DIC$_i$ and DIC$_{\text{ocean}}$ 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) ($\frac{S_i}{S_{\text{ocean}}} \times \text{DIC}_{\text{ocean}}$) represents the oceanic DIC component. 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 (alongshore) of the inner shelf (140–180 µmol kg^{-1}) and lowest on the outer shelf (−10 to 50 µmol kg^{-1}) (Fig. 11). Like DOC, the total excess DIC shows negative correlation
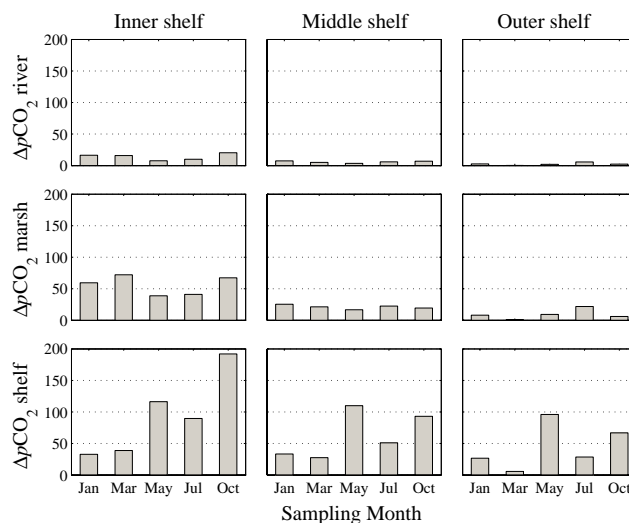
Fig. 8. Seasonal changes of area-averaged ΔpCO$_2$ (river), (referenced to 23.11 °C), ΔpCO$_2$(marsh), and ΔpCO$_2$(shelf).
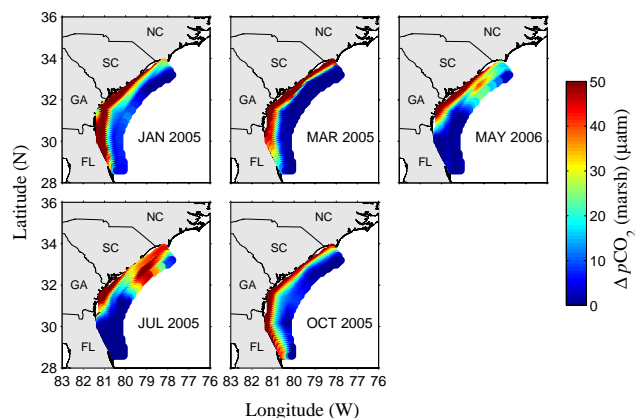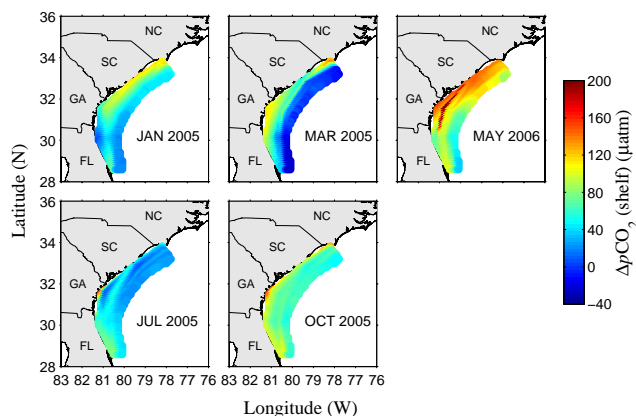

Fig. 9. Spatial distributions of ΔpCO$_2$(marsh) (referenced to 23.11 °C). Due to a lack of DIC data, ΔpCO$_2$(marsh) in December 2005 is not presented. The colored contours are from triangle-based liner interpolation.

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 on the inner shelf and decreased 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 with that from the open ocean, a larger proportion of the terrestrial DIC exists in the form of aqueous CO$_2$. As a result, the input of terrestrial DIC plays a critical role in elevating CO$_2$ concentrations in continental shelf waters. Terrestrial sources increase
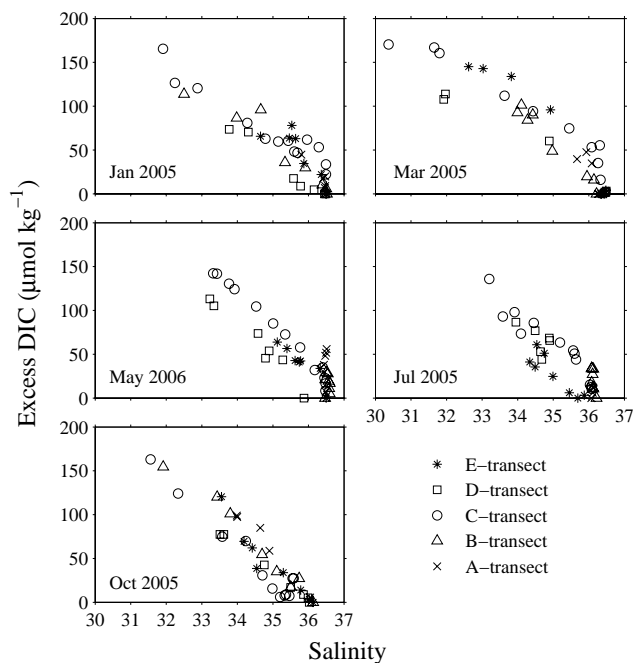
Fig. 10. Spatial distributions of $\Delta p\mathrm{CO}_2$(shelf) (referenced to 23.11 °C). Due to a lack of DIC data, $\Delta p\mathrm{CO}_2$(shelf) in December 2005 is not presented. The colored contours are from triangle-based liner interpolation.

Fig. 11. Surface water total excess DIC (in excess of DIC from oceanic sources) 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 (i.e., DOC in excess of that from oceanic sources) vs. salinity in March, July, October 2005 and May 2006 in the South Atlantic Bight. Due to a lack of data, excess DOC in January and December 2005 was not calculated.

nearshore $p\mathrm{CO}_2$ 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 to varying extents on the shelf as part of the shelf NEM.

Rivers discharging to the SAB enhance $p\mathrm{CO}_2$ in shelf waters by delivering freshwater 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 $p\mathrm{CO}_2$ in these river-dominated estuaries is as high as ~ 4000 µatm compared with only about ~ 400–600 µatm on the continental shelf (Cai and Wang, 1998; Jiang et al., 2008b).

Salt marshes contribute to $p\mathrm{CO}_2$ 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 *Spartina alterniflora*, which has among the highest primary productivity of any ecosystem (~ 1100 to 2250 g C 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
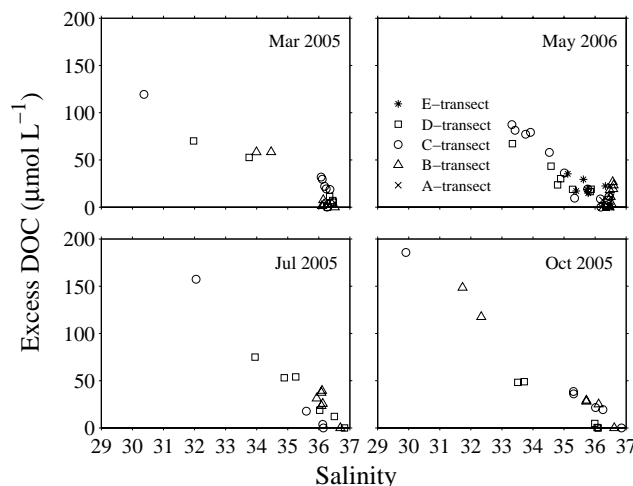
shelf waters and sediments will further increase the nearshore $p\mathrm{CO}_2$. Previous studies have shown that most nutrients entering the SAB occur in organic form that must be remineralized before they may be taken up by phytoplankton (Dunstan and Atkinson, 1976; Hanson et al., 1990; DeAlteris, 2007). The potential importance of this pathway in enhancing $p\mathrm{CO}_2$

on the proximal SAB is supported by the positive correlation between TG-corrected pCO$_2$ and excess DOC (figure not shown).

4.3 Seasonal changes of CO$_2$ inputs to the proximal SAB

Seasonally, CO$_2$ from the SAB rivers and salt marshes is largely related to river discharge rates, and greater amounts of 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 higher ΔpCO$_2$(river) and ΔpCO$_2$(marsh) during January and March 2005 (high flow seasons, Jiang, 2009) than in May 2006 and July 2005 (low flow seasons) (Fig. 8).

Based on the findings from the present study, CO$_2$ production from within shelf waters (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 inner shelf 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 CO$_2$ released from heterotrophic processes in summer may be counterbalanced by greater CO$_2$ uptake due to aquatic primary production at this time of the year (Verity et al., 2002). The results of ΔpCO$_2$(shelf) suggest that the shelf is more likely to be heterotrophic (i.e., net release of CO$_2$) during summer and fall (May 2006, July and October 2005), and relatively more autotrophic (i.e., net uptake of CO$_2$) during winter and spring (January and March 2005) (Fig. 8). This is confirmed by the δ^{13} values of DIC in the proximal SAB, which became increasingly depleted between spring and fall (DeAlteris, 2007). The relatively lower CO$_2$ production during July 2005 may be further related to a Gulf Stream intrusion, which increased biological production and counterbalanced the DIC production.

5 Conclusions

Analyses of the DIC, DOC, and pCO$_2$ data in the SAB demonstrate how temperature, air–sea gas exchange, and terrestrial inputs control sea surface pCO$_2$ on the continental shelf. Terrestrial sources increase the nearshore pCO$_2$ 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 (i.e., shelf NEM). This mechanism is the most likely explanation for findings of the proximal SAB (inner shelf) being a source of atmospheric CO$_2$ ($+1.2\,\mathrm{mol\,m^2\,yr^{-1}}$), and the distal SAB (middle and outer shelf) being a sink of $-1.3\,\mathrm{mol\,m^2\,yr^{-1}}$ (Jiang et al., 2008a). In particular, decomposition of marsh- and river-derived organic carbon is the most important factor in maintaining the high pCO$_2$ on the inner shelf during the fall.

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