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## Elemental and Isotopic Characterization of Organic Matter and Carbon in the U.S South Atlantic Bight

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**ELEMENTAL AND ISOTOPIC CHARACTERIZATION  
OF ORGANIC MATTER AND CARBON  
IN THE U.S. SOUTH ATLANTIC BIGHT**

**A Thesis**

**Presented to**

**The Faculty of the School of Marine Science**

**College of William & Mary**

**In Partial Fulfillment**

**Of the Requirements for the Degree of**

**Master of Science**

**By:**

**Jennifer A. DeAlteris**

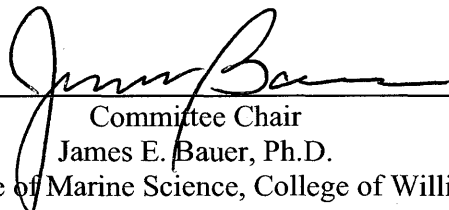
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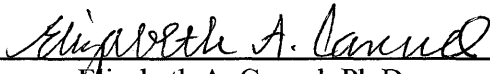
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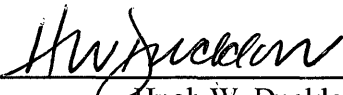
Master of Science


  
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## ABSTRACT

Ocean margins are dynamic systems linking the terrestrial and ocean realms. These transitional environments determine the fate of land-derived materials as they enter the ocean. While ocean margins are a relatively small part of the global ocean area (less than ~10% for continental shelves), they comprise a disproportionately large fraction of ocean primary productivity (~20%) and receive significant inputs of organic and inorganic river-borne materials from land. The complexity and variability of individual ocean margin systems therefore requires that a variety of factors be assessed when considering the relevant sources and fates of carbon and organic matter (OM), and the transfer of these materials through margins to the open oceans. In addition, physical and biogeochemical processes must be evaluated on relevant spatial and temporal scales in ocean margins in order to establish the net trophic status of these systems.

In the present study, a regional-scale geochemical approach was used to assess OM sources and utilization in the South Atlantic Bight (SAB). The primary tools used include: 1) elemental composition and stoichiometry to assess sources and recycling of OM, 2) natural abundance carbon isotopes to examine sources and ages of OM in the SAB, as well as adjacent rivers, estuaries and salt marshes, and 3) experimental dark incubations to evaluate the time frames of dissolved OM (DOM) decomposition in the SAB, and the elemental and isotopic changes that occur during DOM remineralization. In this way, a more integrated assessment of the sources and cycling of OM in the SAB ocean margin may be made compared to using any of these approaches by themselves.

Inner shelf stations received significant inputs of dissolved and particulate organic carbon (DOC and POC, respectively) from river, estuarine and marsh sources as seen in the across-shelf concentration gradients and isotopic signatures of both of these bulk pools. The dominant pattern of DOC sources across the SAB was younger terrestrial forms on the inner shelf, grading to older marine forms offshore. In contrast, the dominant pattern of POC sources across the SAB was older terrestrial forms inshore, transitioning to younger marine forms in mid- and outer-shelf waters. In addition, DOM in the SAB was significantly depleted in N and P compared to the Redfield ratio, suggesting significant DOM recycling throughout the SAB. Distributions and isotopic signatures of carbon and OM were used in a dual isotope mass balance model to estimate relative contributions of different potential sources. These estimates suggest that river and salt marsh materials measurably influenced the composition of DOC, POC and DIC (up to 80%, 50% and 50%, respectively) pools and their cycling on the inner SAB shelf.

Results from this study also illustrate year-round across-shelf gradients in other carbon and OM distributions and associated parameters, and OM recycling in surface waters. In addition, temporal changes in the magnitudes and sources of terrestrial inputs to surface waters of inner shelf sites from winter/spring (March) to summer/fall (July and October) may also affect C and OM processing differently on the mid- and outer shelf compared to the nearshore SAB. Finally, several lines of evidence presented in the current study are consistent with the classification of the SAB as a heterotrophic ocean margin as well as with the “marsh CO<sub>2</sub> pump” hypothesis.

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## INTRODUCTION & BACKGROUND

### *The Role of Ocean Margins in the Ocean Carbon Cycle*

Continental shelf and slope environments play a critical role in the transfer and transformation of carbon and organic matter between land and ocean, and may support as much as half of the ocean's biogeochemical fluxes in this region (Walsh 1991). At present, the amounts and forms of carbon entering the open ocean from ocean margins are poorly constrained and inadequately incorporated into models and budgets of the ocean and global carbon cycles (Gattuso et al. 1998). In addition, autochthonous production in margins is supplemented by terrestrial materials, both as inorganic nutrient and allochthonous organic matter (OM) inputs (Hedges 1992; Gattuso et al. 1998; Jickells 1998). Riverine organic C inputs (ranging from ~0.4 to 0.8 Gt C yr<sup>-1</sup>; Meybeck 1993; Richey 2004) are approximately equal to the amount of new production (~0.8 Gt C yr<sup>-1</sup>) in ocean margins and contribute ~13% of the C to primary production (6.2 Gt C yr<sup>-1</sup>) occurring in these systems (Chen 2004). However, the stoichiometry, character, age and reactivity of allochthonous forms of OM in ocean margins are likely to be very different (Hopkinson et al. 1998), and may be represent key factors controlling the net trophic status of a given margin (Smith and Hollibaugh 1993).

The diverse nature of land-ocean boundaries requires that a number of different types of ocean margin systems (representing a variety of physical, nutrient, climatological regimes, etc.) be examined in order to assess both the magnitudes of the relevant fluxes, as well as the processes regulating these fluxes (Gattuso et al. 1998; Ducklow and McCallister 2004; Borges 2005; Cai et al. 2006). Recently, ocean margins have been classified on the basis of their productivity, fluxes of materials, stratification, regional geomorphology, or latitude (i.e., tropical, temperate or polar/sub-polar systems; Borges 2005; Borges et al. 2005; Cai et al. 2006). Thus, single-system estimates may be neither representative of all margin systems nor sufficient for ocean carbon budgets and models (Smith and Hollibaugh 1993; Borges 2005).

### ***Net Trophic Status and Ocean Margin Carbon Fluxes***

The net trophic status of an ecosystem describes the balance of net production or consumption of organic C by a system (Smith and Mackenzie 1987) and may be evaluated by comparing rates of OM production (P) and respiration (R) through time as they are sustained by the supply of metabolites, inorganic nutrients or allochthonous OM (Smith and Mackenzie 1987; Smith and Hollibaugh 1993; Ducklow and McCallister 2004). Net heterotrophic environments consume more OM than they produce and tend to act as a source of CO<sub>2</sub> to the atmosphere, while net autotrophic systems produce more OM than is respired and usually act as a sink for atmospheric CO<sub>2</sub>. The direction of the air-sea CO<sub>2</sub> flux is determined by the partial pressure (*p*CO<sub>2</sub>) gradient between the two media, and is complicated by the increasing anthropogenic CO<sub>2</sub> enrichment in the atmospheric pool (Gattuso et al. 1998; Ducklow and McCallister 2004). In order to measure organic metabolism on continental shelves globally, information on both the rates of primary production and respiration are needed (Smith and Mackenzie 1987; Ducklow and McCallister 2004). Smith and Hollibaugh (1993) estimated that these rates are approximately equal on the continental shelves, while Gattuso et al. (1998) have calculated shelves to be net autotrophic systems, exporting ~2.1 Gt C yr<sup>-1</sup> OM.

In order to assess the factors contributing to net trophic status and the balance of P vs. R, the sources and reactivity of allochthonous sources of OM must also be considered (Gattuso et al. 1998; Duarte and Prairie 2005). Global fluvial export of dissolved and particulate organic carbon (DOC and POC, respectively) to the coastal oceans is currently estimated at ~0.4-0.8 Gt C yr<sup>-1</sup> (Meybeck 1993; Hedges et al. 1997; Richey 2004) with total carbon (organic plus inorganic) inputs estimated at ~1.1 Gt C yr<sup>-1</sup> (Gattuso et al. 1998; Sabine et al. 2004). The fates of this allochthonous OM include burial in deltaic and shelf sediment (i.e., POC), respiration to inorganic components, or export to the open ocean (Smith and Hollibaugh 1993; Hedges et al. 1997; Opsahl and Benner 1997). These

coastal inputs would be predicted to affect the balance of P:R and hence, the trophic status of margin systems locally, if not globally (Smith and Hollibaugh 1993). The composition and structure of marine microbial communities may play a role in regulating the accumulation and subsequent remineralization of OM of both allochthonous and autochthonous origin (Carlson 2002). Biogeochemical cycles in the coastal zone are altered by anthropogenic increases of organic matter and nutrients via river discharge resulting in losses of C, N, and P from land and a gain of C, N, and P in the coastal and open ocean reservoirs (Rabouille et al. 2001; Andersson and Mackenzie 2004; Lerman et al. 2004).

However, there is still much uncertainty about the reactivity of allochthonous terrestrial and riverine OM (Hedges et al. 1997; Moran et al. 1999; Raymond and Bauer 2001b), as well as the turnover processes controlling the elemental stoichiometry of OM in margin environments (Hedges et al. 1997; Hopkinson et al. 2002). For example, the “quality” of OM, e.g., its stoichiometry and biochemical composition, may affect the trophic balance of the system, in that OM with a higher C:N:P will release relatively more C when remineralized than lower C:N:P OM which would release proportionately more N and P that would be available for additional phytoplankton growth. Similarly, certain biomolecules (e.g., amino acids, proteins, nucleic acids, etc.) have been found to be relatively more reactive than others (e.g., carbohydrates, lipids, etc.) and tend to be preferentially utilized by heterotrophic bacteria (Benner 2002; Killops and Killops 2005).

### ***Present Assessment of Trophic Status for Different Ocean Margins***

As a result of the diversity and complexity of shelf systems, their role(s) in the carbon cycle has yet to be quantified with any certainty (Chen 2004). Recently, studies have shifted to using sea surface CO<sub>2</sub> uptake or release as an indicator of system level trophic status (Smith and Hollibaugh 1993; Ducklow and McCallister 2004), in contrast to previous studies that employed production (P) and respiration (R) rate measurements

solely (del Giorgio et al. 1997; Duarte and Agusti 1998; Williams 1998). Air-sea fluxes of CO<sub>2</sub> indicate if a region is acting as a net source or sink of CO<sub>2</sub> to the atmosphere and also may accurately reflect the metabolic balance between P and R in some regions (Frankignoulle and Borges 2001; Duarte and Prairie 2005). However, because the air-sea flux is influenced by physical processes (e.g., temperature), biological processes (production or consumption of OM), inputs and export of both organic and inorganic carbon with neighboring systems as well as accumulation of anthropogenic CO<sub>2</sub>, this interpretation should be used with care for evaluating net trophic status (Ducklow and McCallister 2004). Presently, synthesis of air-sea CO<sub>2</sub> fluxes in margin systems is based on regional differences and comparisons, such as adjacent coastal systems, margin morphologies, ocean circulation patterns, and latitudinal divisions (Borges 2005; Cai et al. 2006). On the basis of these types of evaluations, both Borges (2005) and Cai et al. (2006) conclude that in general, the coastal ocean acts as a net CO<sub>2</sub> sink in high and temperate latitudes, and as a net CO<sub>2</sub> source in tropical latitudes on an annually integrated basis.

Borges (2005) further examined differences between systems by comparing the carbon budgets of the South Atlantic Bight (SAB) and the North Sea. He concluded that while both are heterotrophic systems, respiring more OM than they produce, the SAB is a source of CO<sub>2</sub> to the atmosphere because it is permanently well mixed in contrast to the North Sea which is a sink for atmospheric CO<sub>2</sub> because it is seasonally stratified and can export DIC more efficiently to the ocean (Borges 2005). Such a finding is a reminder of the necessity to consider both physical and biological factors, as well as the variability of  $\Delta p\text{CO}_2$  in time and space (Ducklow and McCallister 2004). The need for a more extensive spatial and temporal observational network of margin systems is also evident from findings such as these (Cai et al. 2006).

### *Evaluating Organic Matter Sources and Cycling in Ocean Margins*

A number of approaches have been developed for tracing the sources and fates of autochthonous and allochthonous OM in marine systems, including elemental composition and stoichiometry (Jackson and Williams 1985; Hopkinson et al. 1997), organic biomarkers (Meyers-Schulte and Hedges 1986; Macko 1994; Hedges et al. 1997; Benner 2004), and stable and radio-isotope natural abundances (Fry and Sherr 1984; Michener and Schell 1994; Bauer 2002). It should be noted that each of these approaches has advantages and disadvantages, depending on the processes and time scales being examined.

With respect to elemental stoichiometry, the extent of coupling between dissolved organic C, N, and P is critical to evaluating the inputs, decomposition and transport of OM throughout a given system (Hopkinson et al. 2002). In the ocean, terrestrial OM is thought to be rapidly degraded, but identifying the processes and the associated factors controlling them has proved challenging (Hedges et al. 1997). Stoichiometric variations of OM composition in the coastal ocean are believed to be related to its sources (terrestrial vs. marine), as well as decomposition by biotic (bacterial remineralization) (Hopkinson and Vallino 2005), abiotic (photochemical; Miller and Zepp 1995), or a combination of both processes (Amon and Benner 1996; Miller and Moran 1997; Obernosterer and Benner 2004; McCallister et al. 2006).

Vascular plants exhibit many bulk chemical and isotopic properties that distinguish them from marine organisms (Hedges et al. 1997). Organic substances unique to vascular land plants characteristically contain high concentrations of nitrogen-free biomacromolecules, such as lignin (Hedges et al. 1997; Killops and Killops 2005). It is possible to trace the fate of terrestrial organic matter in marine ecosystems based on the presence of lignin-derived compounds, thus providing evidence on the presence and quantitative importance of land-derived vascular plant detritus in marine systems (Moran et al. 1991; Mannino and Harvey 2000). The application of lipid biomarker compounds

can provide further source-specific information about allochthonous and autochthonous inputs and the diagenetic states of DOM and POM in coastal systems (Shi et al. 2001; McCallister et al. 2006).

Natural abundance isotope signatures may also provide an excellent means of tracing sources of bulk OM (both particulate and dissolved pools) in ocean margin waters (Hedges et al. 1997; Peterson 1999), as well as the DIC derived from its respiration (Coffin et al. 1994).  $\delta^{13}\text{C}$  is useful for determining dominant sources to an OM pool, such as upland  $\text{C}_3$  plants ( $\delta^{13}\text{C}=-26$  to  $-30\text{‰}$ ),  $\text{C}_4$  marsh grasses ( $\delta^{13}\text{C}=-13$  to  $-17\text{‰}$ ), and marine phytoplankton ( $\delta^{13}\text{C}=-20$  to  $-22\text{‰}$ ; Fry and Sherr 1984; Boutton 1991b; Coleman and Fry 1991; Libes 1992; Michener and Schell 1994). Natural radiocarbon ( $\Delta^{14}\text{C}$ ) provides an additional degree of sensitivity to end member identification as it has a much greater dynamic range of values as well as adding a time element to the sources and aging OM (Raymond and Bauer 2001c; Bauer 2002; McCallister et al. 2004). A dual carbon isotope approach (i.e., using  $\Delta^{14}\text{C}$  and  $\delta^{13}\text{C}$ ) allows C pools to be traced even more specifically than single isotopes or by using stable isotopes of multiple elements (e.g., C, N, and S) which may “generalize” OM pool sources (Raymond and Bauer 2001c; Bauer 2002).  $\Delta^{14}\text{C}$  may further provide information on the residence times of OM and when combined with  $\delta^{13}\text{C}$  isotope data, and may help to overcome problems associated with source overlap from using  $\delta^{13}\text{C}$  exclusively (Raymond and Bauer 2001c; Bauer 2002).

In a similar manner, the dual isotope method may also more accurately identify sources of respired OM contributing to DIC. For example, both  $\delta^{13}\text{C}$ -DIC and  $\Delta^{14}\text{C}$ -DIC, when plotted against a conservative tracer such as salinity, may be used to generate a conservative isotopic mixing model, against which observed  $\delta^{13}\text{C}$ -DIC and  $\Delta^{14}\text{C}$ -DIC may be compared (Spiker 1980; Coffin et al. 1994; Raymond and Bauer 2001c). Deviations from the mixing line may be used to infer net heterotrophy or autotrophy, as well as the isotopic signatures of OM respired in different systems (Spiker 1980; Coffin et al. 1994).

In the present study, a regional-scale geochemical approach was used to assess OM sources and utilization in the SAB. The primary tools used include: 1) OM elemental composition and stoichiometry, 2) dual carbon isotopes to examine changes in the geochemical reactivity of OM being exported to and utilized in the SAB ocean margin, and 3) experimental dark incubations to evaluate the timeframes of DOC decomposition in the SAB, and the elemental and isotopic changes that occur during decomposition. In this way, a more integrated assessment of the sources and cycling of OM in ocean margins may be made compared to using any of these approaches alone.

## RESEARCH OBJECTIVES

The primary objective of this study was to assess the potential factors contributing to net heterotrophy in the SAB ocean margin by examining the spatial and temporal biogeochemical variability in the carbon and OM pools there using: i) C, N, and P distributions, ii) elemental stoichiometry of OM, and iii) natural abundance carbon isotope ( $^{13}\text{C}$  and  $^{14}\text{C}$ ) distributions in bulk organic and inorganic carbon pools. Three hypotheses were posed in an attempt to address these issues:

### *Hypothesis 1*

The concentrations and elemental ratios of DOM and POM in the SAB will vary as a function of: i) terrestrial and marsh sources being transported offshore and mixing with autochthonous shelf-derived OM, and ii) differences in the relative remineralization of the C, N and P components of OM in different areas of the SAB.

- C:N and C:P ratios in DOM and POM will increase as N- and P-depleted OM from rivers and marshes mixes with N- and P-enriched material offshore, and as heterotrophic bacteria preferentially remineralize the more reactive N and P components of OM.

### *Hypothesis 2*

The  $\delta^{13}\text{C}$  and  $\Delta^{14}\text{C}$  signatures of DOM, POM and DIC will vary spatially and temporally as a function of the changing end member sources and remineralization of DOM and POM throughout the SAB.

- $\delta^{13}\text{C}$  signatures of the major carbon pools will exhibit greater contributions from  $\text{C}_3$  and  $\text{C}_4$  terrestrial plant materials in shallower, fresher inshore waters, while offshore and deeper waters will have a stronger marine planktonic isotopic signal. The  $\Delta^{14}\text{C}$  signature will reflect similar source signatures as well as the relative



ages of materials as younger river and marsh derived DOM is degraded and mixed with older marine DOM (the opposite trend is predicted for POM).

***Hypothesis 3***

The relative reactivity of DOM will vary across the SAB shelf due to differences in OM source composition and age.

- Dark decomposition experiments utilizing SAB surface waters will establish a link between the origin of DOC (i.e., through its  $\Delta^{14}\text{C}$  and  $\delta^{13}\text{C}$  signatures and C:N:P), its reactivity (i.e., through its rates and extents of DOC decomposition) and the preferences of free-living bacteria (i.e., through their utilization of isotopically unique DOC components).

## MATERIALS & METHODS

### *The South Atlantic Bight Study Region – Physical and Biological Setting*

The area defined by the SAB extends from Cape Canaveral, FL to Cape Hatteras, NC, and the width of the continental shelf is variable, ranging from 5 to 120 km offshore (Figure 1). A notable bathymetric feature is the Charleston Bump where the 500 m isobath extends to about 200 km offshore. This irregularity has been found to interfere with Gulf Stream flow causing recirculation eddies in its lee (Lee et al. 1991; Boicourt et al. 1998), allowing for nutrient rich meanders to intrude onto the SAB shelf. The mean circulation in the SAB is primarily driven by seasonal atmospheric variations and fluctuations in the position of the Gulf Stream (Boicourt et al. 1998). Tidal range is ~1-3 m with the maximum range observed off Georgia, and this tidal forcing controls seawater flow on the inner shelf (Atkinson and Menzel 1985). The SAB shelf is weakly stratified in the summer and fall months, while in the winter and spring it is well mixed (Menzel 1993).

Mixing of water masses in the SAB occurs in two dynamic frontal zones (Pomeroy et al. 2000). The first occurs over the inner shelf around the 15 m isobath, and is defined by the mixing of estuarine water with more saline coastal ocean water (Menzel 1993; Pomeroy et al. 2000). This creates turbid particle-rich waters where enhanced OM remineralization may occur (Yoder 1985; Menzel 1993). Beyond this mixing zone are nutrient-poor waters on the mid- and outer shelves, bordered by the Gulf Stream to the east and a second frontal zone (Pomeroy et al. 2000). Nutrient-rich Gulf Stream waters occasionally intrude onto the shelf due to baroclinic instability, acting as a “nutrient pump” and allowing mesoscale phytoplankton blooms to occur (Lee et al. 1991). Lee et al. (1991) calculated that these blooms were responsible for  $\sim 4.3 \text{ Tg C yr}^{-1}$  in new production on the outer shelf. It was also suggested that there is a cascade removal process of the upwelled water mass during the winter due to cooling via heat exchange.

with the atmosphere and subsequent density increases of the water mass, thus removing the phytoplankton C off the shelf to the Gulf Stream (Yoder and Ishimaru 1989).

Because the SAB is a subtropical ocean margin with weakly stratified conditions, it does not undergo a typical, distinct spring bloom like more highly stratified temperate margins, such as the Mid Atlantic Bight (MAB; Menzel 1993). Also in contrast to the MAB, benthic primary production (BPP) in the SAB is significant (averaging  $\sim 400 \text{ mg C m}^{-2} \text{ d}^{-1}$ ) on the mid shelf and accounts for almost half of the total primary production (averaging  $\sim 1082 \text{ mg C m}^{-2} \text{ d}^{-1}$ ) occurring in the system (Jahnke et al. 2000). In subsequent studies, this same group determined that sediments are responsible for half of the total metabolic carbon turnover, implying that sedimentary metabolism is a major component of overall SAB shelf biogeochemical cycling (Jahnke et al. 2005).

Water column primary production in the inner SAB has been measured as  $\sim 73\%$  of community metabolism ( $759 \text{ g C m}^{-2} \text{ yr}^{-1}$ ; Hopkinson 1985), indicating that sources of OM other than autochthonously produced material must supplement respiration there (Hopkinson 1985; Menzel 1993; Cai et al. 2003). Stratified conditions further allow for increased production of bacterioplankton biomass in SAB surface waters (Hanson et al. 1988), which coincides with increased DOC concentrations (Moran et al. 1991). Bacterial growth efficiency (BGE) in the SAB decreases with increasing distance offshore; however, similar isotope dilution studies report a variety of BGE values. Extremely high BGE values, ranging from 91% on the mid-shelf to relatively low efficiencies (55%) close to the Gulf Stream were reported by Pomeroy et al. (2000;  $^3\text{H}$ -leucine incorporation experiments); while Griffith et al. (1990) reported much lower BGE measurements, varying from 11% in Georgia estuaries, to 2% in shelf waters ( $^3\text{H}$ -thymidine incorporation experiments). Free-living bacteria in coastal waters are estimated to be responsible for 80-99% of the pelagic community respiration (Griffith et al. 1990). The combined effect of high bacterial efficiency and low phytoplankton

biomass results in a generally smaller number of trophic levels in the waters of the SAB than expected (Pomeroy et al. 2000).

### ***Trophic Status of the South Atlantic Bight – Current Understanding***

The Georgia coastal system has been well studied for over 50 years by a number of researchers. Early studies in the 1960's resulted in the controversial “outwelling hypothesis” by Odum (1968), which proposed that salt marsh-dominated estuaries export significant quantities of nutrients and organic detritus to the inner shelf. Several studies have attempted to evaluate the export of salt marsh POM to the SAB using stable isotopes, but results suggested instead the dominance of marine phytoplankton sources (Haines 1976; Peterson and Howarth 1987). POM from tidal creeks and estuaries was further found to be derived from both salt marshes and marine phytoplankton, but not neighboring upland vegetation and soils (Peterson and Howarth 1987).

Dissolved lignin phenols in SAB shelf waters were found to have a negative linear correlation with salinity, implying that terrestrial OM that is exported to the shelf may behave conservatively in this system (Moran et al. 1991; Hopkinson et al. 1998). Moran et al. (1991) also suggested that less than one third of the bulk DOC in the SAB is terrestrially derived based on the lignin phenol concentrations, but this value is significantly influenced by freshwater discharge. Thus, in contrast to the stable isotope findings, the lignin phenol findings are consistent with Odum's (1968) “outwelling hypothesis”. Part of the discrepancy may be the relatively narrow dynamic range of  $\delta^{13}\text{C}$  as an indicator of terrestrial, marsh and shelf sources of organic matter as well as overlapping  $\delta^{13}\text{C}$  signatures of these sources.

In the 1980's, studies of carbon flow within SAB marshes and nearshore waters found that on an annual basis more carbon was respired ( $759 \text{ g C m}^{-2}$ ) than was fixed by primary producers ( $539 \text{ g C m}^{-2}$ ) and that only in November did photosynthesis exceed respiration (Figure 2; Hopkinson 1985). The data further showed a relationship between

respiration and temperature, but not between respiration and photosynthesis which has been interpreted as suggesting a dependence on allochthonous OM in the SAB nearshore region (Hopkinson 1985).

More recently, research on the trophic status in this region has focused not only on the flux of OM, but on the transfer of dissolved inorganic carbon (DIC), alkalinity, and pH from salt marshes to the coastal ocean (Cai and Wang 1998; Wang and Cai 2004; Wang et al. 2005). Work in the Duplin River, a marsh dominated estuary, quantified the inorganic carbon mass balance and led to the idea of a “marsh CO<sub>2</sub> pump”, referring to the annual process of CO<sub>2</sub> accumulation and release in marshes and associated apparent net heterotrophy in the estuary (Wang and Cai 2004). This seasonal CO<sub>2</sub> cycle in the SAB “begins” in the spring and early summer with the accumulation of primary producer biomass via photosynthesis in salt marshes, followed by an export phase in the late summer and fall when primary production decreases and respiration increases, releasing DIC and DOC to the adjacent estuaries (Wang and Cai 2004). A similar seasonal cycle is evident in the air-sea CO<sub>2</sub> fluxes in the coastal waters of the central SAB (Figure 3; Cai et al. 2003). From these and other findings, a carbon transport model was developed for the region, indicating that the SAB is net heterotrophic during these studies, acting as a source of CO<sub>2</sub> to the atmosphere and exporting DIC (and possibly DOC) to the adjacent open ocean (Cai et al. 2003; Wang et al. 2005).

#### ***2005 South Atlantic Bight Field Program: Whole-Shelf Sampling***

In order to address the objective and hypotheses for this project, three research cruises were conducted in 2005 in the SAB. In March and July, work was conducted on the *R/V Cape Hatteras*, while the *R/V F.G. Walton Smith* served as the platform for the October cruise. Sampling was conducted at three stations along each of five cross-shelf transects (Table 1 and Figure 4) and stations were chosen to be generally representative of the inner- and mid shelves, and outer shelf/inner slope waters. A SBE 32 Carousel

Water Sampler (rosette), equipped with 10% HCl-cleaned 30L Niskin bottles with external spring closures was used to collect water samples from a series of depths (approximately 2, 50, 150, 300, 500 m depth, and ~5 m above the seafloor) while a SeaBird CTD collected continuous hydrographic information.

All seawater samples were processed in a clean van located on the deck of the ship. Whole, unfiltered water samples were collected for dissolved inorganic carbon (DIC) isotopes in duplicate gas-tight 125 mL serum bottles (Wheaton) poisoned with  $\text{HgCl}_2$  and stored in the dark at room temperature. The remainder of the sample was filtered through pre-cleaned 47 mm Whatman QMA quartz fiber filters (baked at 500°C for 4 hours) for DOC (i.e., OM in the filtrate) and POC (i.e., OM collected on filters) isotopic analyses. Duplicate DOC isotope samples were filtered into 1L pre-cleaned glass amber bottles (baked at 500°C for 4 hours), and frozen at -20°C. The volume of water filtered was recorded and all DOC and POC samples were frozen at -20°C until analysis. At mid- and outer shelf stations, only one filter was needed per depth due to the low particulate loads, however, at inshore stations where there were increased particulate loads, multiple filters were necessary. Filtered samples for nutrient ( $\text{NO}_x^-$ ,  $\text{NH}_4^+$ , DON,  $\text{PO}_4^{3-}$ , and DOP) and DOC concentrations were collected in duplicate in 125 mL acid pre-cleaned Nalgene HDPE bottles and also preserved by freezing at -20°C.

### ***DOM Dark Decomposition Experiments***

Surface water samples from central SAB transect C were collected in duplicate (designated as A and B) on all cruises and immediately filtered through QMA filters (baked at 500°C for 4 hours) into clean 20L polycarbonate carboys (Diamond Springs distilled water containers). The carboys were subsequently maintained in the dark at a stable room temperature (~22°C) and sampled periodically. Triplicate sub-samples for DOC concentrations were collected weekly for the first month, and subsequently collected monthly for six months and bimonthly for up to a year or until the DOC

concentration decreases by ~10-20% or more of the original concentration (Hopkinson et al. 1997) in order to allow for robust decay rate coefficients and isotopic mass balances to be calculated. At the conclusion of the incubations, final nutrient samples were collected in duplicate to quantify the percent of DON and DOP utilized, calculated as the difference between initial and final sample concentrations divided by the initial concentration (Hopkinson et al. 1997), and final DOC isotope samples were collected in duplicate to determine the isotopic signatures of the reactive and refractory DOC components (Raymond and Bauer 2001a). Decay rate coefficients (k) were calculated as a first order reaction, where concentration is related to the decay rate and time by the equation:

$$C = C_0 * e^{-kt} \quad (\text{Eqn. 1})$$

Where  $C_0$  is the initial concentration, t is time, and k is the decay rate coefficient (Hopkinson et al. 1997).

### ***2006 Field Program: River and Marsh End-Member Sampling***

In order to use dual isotope mixing models for assessing the sources contributing to the OM and C pools in the SAB, the isotopic composition of appropriate major end members must be sufficiently constrained (Raymond and Bauer 2001c; Bauer 2002). “Terrestrial” end members chosen for evaluation in this study included six rivers and two sites in a Georgia coastal salt marsh system. Rivers were sampled in July 2006, and included the St. Johns (FL), Altamaha (GA), Savannah (GA), Cooper (SC), Pee Dee (SC), and Cape Fear (NC) Rivers. These rivers were chosen on the basis of their high (i.e., relative to other SAB rivers) yearly discharges (Menzel 1993); USGS streamflow statistics (<http://www.usgs.gov/>) were used to observe seasonal trends in discharge (shown in Figure 5A-D). The Altamaha, Savannah, Pee Dee and Cape Fear Rivers are considered to be piedmont rivers, characterized by high carbonate contents and higher pH values (Menzel 1993; Dame et al. 2000). However, the Cooper and St. Johns Rivers are

characterized as “blackwater” rivers with lower pH values and high humic concentrations (Moran et al. 1999; Dame et al. 2000).

Sample sites for terrestrial sources, both riverine and salt marsh, are listed in Table 2. Samples for POC, DOC, and DIC isotope measurements, as well as dissolved inorganic and organic nutrient samples, were collected from these rivers at sites upstream from the point of saltwater intrusion and away from any major industrial activities. The Savannah and Great Pee Dee Rivers were sampled in completely fresh water portions ( $S < 1$ ), while the Cape Fear, Altamaha and St. Johns Rivers were moderately saline ( $S < 10$ ). Due to limited accessibility to the Cooper River at upstream portions, an estuarine sample ( $S \sim 25$ ) was collected from Charleston Harbor. Coastal salt marshes of GA were characterized using water samples obtained from tidal salt marsh creeks on the Sapelo River and Hudson Creek (at the “Marsh Landing”, Georgia Coastal Ecosystems LTER research site). All river and marsh tidal creek samples were collected from docks or bridges using a combination of carboy and pump sampling methods. Water samples were processed in the same manner as described above for SAB cruise samples.

The other major end-members used in this study included shelf primary production and Gulf Stream waters. The isotopic signature of contemporary shelf primary production was estimated using the DIC isotopic signatures after correcting for  $^{13}\text{C}$  isotope fractionation by phytoplankton ( $-19\%$ ; Bauer et al. 2002). Benthic diatoms were also considered as a potential end member to this system, but collection of these organisms was not possible during the shelf cruises in 2005. It was assumed that benthic plankton would have a similar isotopic signature to water column phytoplankton if they are utilizing water column DIC. However, if benthic plankton utilize porewater DIC, then they may have an isotopically distinct signature from water column phytoplankton and this represents a potential source of error to the isotopic mass balance analyses. The Gulf Stream signature of DOC and POC was characterized by deep outer shelf/slope waters ( $> \sim 400$  m) collected during the regular cruise periods.



### ***Laboratory and Analytical Methods***

Samples for  $\Delta^{14}\text{C}$  and  $\delta^{13}\text{C}$  measurements of DOC were processed in the VIMS Radiocarbon Laboratory by oxidizing 100-150 mL of sample to  $\text{CO}_2$  using high energy UV irradiation. Prior to oxidation, samples were acidified with phosphoric acid to a pH of 2.5 and sparged with ultra high purity Helium gas to remove DIC, followed by 10 minutes of sparging with ultra-high purity  $\text{O}_2$  gas. Samples were then irradiated with a medium pressure mercury arc UV lamp (2400 W) for 3 hours (Bauer 2002; Bauer et al. 2002). The resulting  $\text{CO}_2$  gas from the oxidized DOC was then isolated and purified cryogenically on a vacuum extraction line, quantified using a calibrated Baratron absolute pressure gauge (MKS Industries), and collected in a 6 mm Pyrex break seal tube. The vacuum system blank and known DOC isotopic standards (including NIST oxalic acid (OX-II) and acetanilide dissolved in UV-irradiated water) were checked regularly using the same UV oxidation procedure.

For POC isotopes, filters were thawed, dried for several hours at  $35^\circ\text{C}$  and exposed for 1-2 days to fresh concentrated HCl to remove carbonates, and then thoroughly dried. The POC filters were then oxidized using CuO and elemental Cu metal at  $850^\circ\text{C}$  in 9 mm evacuated sealed quartz tubes (Sofer 1980; Raymond and Bauer 2001c). The evolved  $\text{CO}_2$  was quantified using the vacuum extraction line procedure described above. Filter blanks were also measured periodically to determine background levels of C, and solid-phase oxalic acid (OX-II) and acetanilide isotopic standards were checked regularly for both C recoveries and isotopic signatures using the same sealed tube combustion methodology.

Serum bottles containing samples for DIC isotopic analysis were acidified to pH 2.5 using 85% phosphoric acid (Boutton 1991a). The resulting  $\text{CO}_2$  was stripped from the sample by sparging with ultra high purity Helium, collected cryogenically, and purified on a vacuum extraction line (Bauer et al. 2002). Quantification and collection of

the CO<sub>2</sub> was performed on the same vacuum extraction line as described above for DOC, but split 10:1 into two separate 6 mm Pyrex break seal tubes. The larger portion was analyzed for  $\Delta^{14}\text{C}$  and the smaller portion for  $\delta^{13}\text{C}$ . A laboratory inter-calibration between the UGA and VIMS laboratories was conducted to ensure high-quality DIC concentration data from independent quantification methods used in each lab as part of this study (i.e., vacuum line extractions at VIMS and Li-Cor 6252 H<sub>2</sub>O/CO<sub>2</sub> analyzer at UGA).

Samples for  $\Delta^{14}\text{C}$  were measured by accelerator mass spectrometry (AMS) at the NSF AMS Facility at the University of Arizona. AMS analytical errors for this study were typically  $\sim\pm 5$  to 10‰. Average standard deviations of  $\Delta^{14}\text{C}$  of replicate samples for the different sample types were  $\pm 15$ ‰ for  $\Delta^{14}\text{C}$ -DOC,  $\pm 11$ ‰ for  $\Delta^{14}\text{C}$ -POC, and  $\pm 6$ ‰ for  $\Delta^{14}\text{C}$ -DIC.  $\delta^{13}\text{C}$  analyses were performed on a Thermo-Finnegan Delta Plus isotope ratio mass spectrometer (IRMS) at Ohio State University having an analytical error typically of  $\pm 0.1$ ‰ or better, and used to correct the  $\Delta^{14}\text{C}$  measurements for fractionation effects. Average standard deviations of  $\delta^{13}\text{C}$  of replicate samples for the different sample types were  $\pm 0.5$ ‰ for  $\delta^{13}\text{C}$ -DOC,  $\pm 0.2$ ‰ for  $\delta^{13}\text{C}$ -POC, and  $\pm 0.1$ ‰ for  $\delta^{13}\text{C}$ -DIC.

Dissolved inorganic N (DIN, as NO<sub>2</sub><sup>-</sup> + NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup>), total dissolved N (TDN), dissolved inorganic P (DIP, as PO<sub>4</sub><sup>3-</sup>), and total dissolved P (TDP) were measured at the VIMS Analytical Service Center using a SKALAR nutrient auto analyzer. Standard reference materials were used as independent checks of the instrument calibration. DIN and DIP concentrations were subtracted from persulfate-oxidized TDN and TDP values, respectively, to obtain the corresponding DON and DOP concentrations. Method detection limits for inorganic components were 0.20  $\mu\text{M}$  for NH<sub>4</sub><sup>+</sup>, 0.27  $\mu\text{M}$  NO<sub>2</sub><sup>-</sup> + NO<sub>3</sub><sup>-</sup>, and 0.18  $\mu\text{M}$  PO<sub>4</sub><sup>3-</sup>. Average standard deviations of duplicate samples for inorganic analytical methods were  $\pm 0.12$   $\mu\text{M}$  for NH<sub>4</sub><sup>+</sup>,  $\pm 0.16$   $\mu\text{M}$  for NO<sub>2</sub><sup>-</sup> + NO<sub>3</sub><sup>-</sup>, and  $\pm 0.04$   $\mu\text{M}$  for PO<sub>4</sub><sup>3-</sup>. For the TDN and TDP pools, method detection limits were 0.76  $\mu\text{M}$  and 0.28  $\mu\text{M}$ , respectively, and average standard deviations of duplicate samples were  $\pm 0.31$   $\mu\text{M}$

and  $\pm 0.05 \mu\text{M}$ , respectively. Propagated errors for the DON and DOP results resulted in averages of  $\pm 0.45 \mu\text{M}$  and  $\pm 0.07 \mu\text{M}$ , respectively. A Shimadzu TOC-5000A was used for DOC analyses using high temperature Pt-catalyzed oxidation. The method detection limit for DOC analysis was  $10.0 \mu\text{M}$  and the mean analytical error of the method was  $\pm 1.4 \mu\text{M}$ . The instrument was checked periodically for accuracy using University of Miami DOC reference samples (provided by the laboratory of Dr. Dennis Hansell; Sharp 2002). In addition to analyses of all duplicate samples collected, instrument precisions of both the SKALAR and Shimadzu were measured by analyzing replicates of 10% of the samples; spikes of 10% of the samples were analyzed to further assess instrument accuracy.

Methodological problems (salinity of the SAB shelf samples mixing with reagents created a high background signal) were encountered in the March 2005 ammonium analyses and these values were not used in calculating DON. An alternate method for ammonium analysis which allowed for high salinity samples was used for all other analyses after this time. Instead, for the March 2005 samples,  $\text{NH}_4^+$  values were estimated later from a subset of March samples (water from 20 DOC isotope sample bottles, ~80% surface waters and ~20% deep water, ~4 stations per transect), which were re-analyzed in December 2006. Results were averaged by transect, resulting in a maximum standard deviation of  $\pm 0.33 \mu\text{M}$  for  $\text{NH}_4^+$  and a maximum propagated error in DON of  $\pm 1.86 \mu\text{M}$  for the March samples.

### ***Data Analysis and Modeling***

Changes in SAB surface concentrations of various analytes are presented using plots made in MATLAB. Regression analysis of various OM and nutrient properties against salinity were used to interpret distributions as well as the level of conservative vs. non-conservative input and/or removal occurring in the SAB. Property-property correlations (including both isotopic and non-isotopic data) were also assessed and

evaluated in a similar manner where appropriate (Jackson and Williams 1985; Hopkinson et al. 1997; Raymond et al. 2004). Following the identification of major spatial and temporal features using these graphs, t-tests and one-way ANOVA (calculated using Excel and MiniTab) were used to identify significant regional and seasonal trends. T-tests were also used for data sets which did not meet the assumption of equality of variance for ANOVAs. For data sets which were not normally distributed, no statistical analysis was conducted beyond reporting of means and standard deviations.

Mixing relationships between fresh water and marine end members may provide insights to the conservative vs. non-conservative behaviors of different solutes. For non-isotopic parameters, the conservative relationship between marine and freshwater end-members is described by a line. However, the conservative distributions of isotope ratios as a function of salinity are described by the equation:

$$X_s = ((F_r * X_r * [DOC]_r) + (F_m * X_m * [DOC]_m)) / [DOC]_s \quad (\text{Eqn. 2})$$

where  $X$  is the isotopic composition ( $\Delta^{14}\text{C}$  or  $\delta^{13}\text{C}$ ) of river ( $r$ ) and marine ( $m$ ) end members and at a given salinity ( $s$ ) (Spiker 1980; Fry 2002; Wang et al. 2004);  $F_r$  and  $F_m$  represent the riverine and marine fractions which can be calculated based on salinity ( $F_r + F_m = 1$ ); and  $[DOC]_r$ ,  $[DOC]_m$ , and  $[DOC]_s$  are the DOC concentrations at riverine and marine end members, and at a given salinity. The  $[DOC]_s$  is calculated based on  $F_r$  and  $F_m$ . The resulting conservative mixing relationships for  $\delta^{13}\text{C}$  and  $\Delta^{14}\text{C}$  are curved because of the weighting of the solute concentrations by the isotopic ratios (i.e.,  $^{13}\text{C}/^{12}\text{C}$  and  $^{14}\text{C}/^{12}\text{C}$ ) used in the  $\delta$  and  $\Delta$  conventions, respectively.

The carbon isotope data were further used in both single and dual isotopic mass balance mixing models to estimate the relative contributions of different OM sources to a given sample and region of the SAB (Kwak and Zedler 1997; Peterson 1999; Raymond and Bauer 2001c; Bauer 2002). Similarly, DIC isotopes were assessed for the contributions of different sources and ages of respired OM contributing to this pool. In order for the isotopic mass balances to be effective, the major end members of the system

must be identified or reasonably assumed, and their isotopic compositions established (Raymond and Bauer 2001c).

For a single isotope 2-source model, the general equation is:

$$X = f_1X_{f1} + f_2X_{f2} \quad (\text{Eqn. 3})$$

where X is the isotopic composition ( $\Delta^{14}\text{C}$  or  $\delta^{13}\text{C}$ ) of components 1 ( $f_1$ ) and 2 ( $f_2$ ) and where  $f_1+f_2=1$  (Kwak and Zedler 1997); the equations are then solved for  $f_1$  and  $f_2$ .

The generalized equation for a two-isotope, 3-source mass balance model is:

$$X = f_1X_{f1} + f_2X_{f2} + (1-f_1-f_2)X_{f3} \quad (\text{Eqn. 4})$$

where X is the isotopic composition ( $\Delta^{14}\text{C}$  or  $\delta^{13}\text{C}$ ) and where  $f_1+f_2+f_3=1$  (Kwak and Zedler 1997; Bauer 2002). The  $\Delta^{14}\text{C}$  and  $\delta^{13}\text{C}$  equations are then solved simultaneously for  $f_1$ ,  $f_2$ , and  $f_3$ .

## RESULTS

### *General Hydrographic Features of the SAB*

Sampling stations for each of the three 2005 cruises are shown along with relevant site information and general physical and hydrographic conditions in Table 1. During the March 2005 cruise, physical conditions of the water column, such as water temperatures, were typical of winter conditions, rather than early spring conditions (Menzel 1993). Surface water temperatures across the shelf showed an onshore-offshore gradient, with cooler waters inshore ( $\sim 10^{\circ}\text{C}$ ), and warmer temperatures offshore ( $\sim 25^{\circ}\text{C}$ ; Table 1), reflecting the presence of Gulf Stream waters. Offshore temperatures decreased with depth ( $> \sim 100$  m) indicating the permanent thermocline (Table 1). In July 2005, surface water temperatures were uniform, creating a smooth, seasonal thermocline profile in deeper shelf and slope waters (Table 1). The upper  $\sim 100$  m of the water column was relatively homogeneously mixed during the October 2005 cruise. Below this depth, the thermocline was maintained, and was more similar to July than March conditions (Table 1).

Salinity varied continuously across the SAB shelf as mixing occurred between the riverine and marine end members. The inner shelf region was characterized by a relatively large range of salinities ( $\sim 30$  to  $36$ ; Table 1) and showed prominent seasonal variations. In March and October 2005, inner shelf stations had the lowest salinity values ( $\sim 30$ ), while in July inner shelf salinities ranged from  $\sim 32$  up to  $36$ . Mid- and outer shelf stations had higher salinities ( $\sim 34$  to  $36$ , and  $\sim 36$ , respectively; Table 1). In deep shelf and slope waters, salinity decreased slightly to  $\sim 35$  where Gulf Stream waters were intruding on to the shelf and slope, similar to conditions observed in previous studies (Lee et al. 1991).

### ***DOC and POC Distributions in the SAB***

DOC concentrations in SAB surface waters (upper ~2 m) during 2005 ranged from a maximum of 240  $\mu\text{M}$  on the inner shelf of C transect in October to ~80  $\mu\text{M}$  on the outer shelf throughout the year (Table 3; Figures 6A-C). In surface waters of the outer shelf, DOC tended to remain at this background concentration during all three sampling periods (Figures 6A-C). For all 2005 cruises (Figures 6A-C), across-shelf DOC concentrations showed significant decreases from inner shelf sites (mean =  $145 \pm 46 \mu\text{M}$ ,  $n=28$ ) to outer shelf sites (mean =  $82 \pm 7 \mu\text{M}$ ,  $n=33$ ; t-test,  $P<0.01$ ). The inner shelf of C transect, especially station C01 adjacent to the outflow of the Sapelo River, was typically the site of highest DOC concentrations, resulting in an across-shelf decrease for all cruise dates (Figures 6A-C). A temporal difference was also evident where DOC concentrations at inner shelf stations (specifically station C01) increased throughout the year, averaging  $130 \pm 24 \mu\text{M}$  in March ( $n=9$ ) and up to  $170 \pm 45 \mu\text{M}$  in October ( $n=10$ ; one-way ANOVA;  $P=0.03$ ). DOC profiles for selected stations showed a consistent decrease to a mean of  $57 \pm 9 \mu\text{M}$  ( $n = 110$ ) at depths  $>100$  m for all sampling periods (Figures 7A-C).

Similar to DOC, surface (upper ~2 m) POC concentrations also showed strong across-shelf decreases (Figures 8A-C). The highest concentrations of POC occurred on the inner shelf, ranging from a high of 698  $\mu\text{g/L}$  at C01 in October to background average of  $44 \pm 35 \mu\text{g/L}$  ( $n = 10$ ) at outer shelf surface stations. In March (Figure 8A), the highest shelf POC concentration, 269  $\mu\text{g/L}$ , occurred at station D01. These elevated POC concentrations at D01 were extended across the shelf (95  $\mu\text{g/L}$  at station D11), creating a non-continuous across-shelf distribution (Figure 8A), that differed from than the other sample dates where high concentrations originated from station C01 (Figures 8B-C). In July and October, POC followed a similar and more “typical” spatial distribution to the DOC concentrations, where POC decreased rapidly from the inner shelf maximum at station C01 towards the mid- and outer shelf stations, resulting in concentrations of ~20

to 50  $\mu\text{g/L}$  at those stations (Figures 8B-C). Also similar to DOC, there was an increase in the overall POC concentration throughout the year (Figures 8A-C) with lowest concentrations in March (even though river discharge was highest during this sample time, Figures 5A-D) and highest concentrations in October.

### ***DOC and POC Isotopic Signatures in the SAB***

Generally, DOC isotopic signatures showed more consistent across-shelf changes than the POC isotopes, which were more variable (Table 4; Figures 9A-C, 10A-C, 11A-C, and 12A-C). Throughout 2005,  $\delta^{13}\text{C}$ -DOC tended to be more depleted (mean =  $-24.0 \pm 0.7\text{‰}$ ,  $n=12$ ) at inner shelf stations (Figures 9A-C), while at mid- and outer shelf stations  $\delta^{13}\text{C}$ -DOC signatures tended to be significantly heavier (mean =  $-22.1 \pm 0.6\text{‰}$ ,  $n=22$ ; one-way ANOVA,  $P<0.01$ ). No distinct seasonal variability in  $\delta^{13}\text{C}$ -DOC between the three sampling periods was noted (Figures 9A-C).

$\Delta^{14}\text{C}$ -DOC displayed strong across-shelf decreases (Figures 10A-C) with inner shelf stations being more enriched (mean =  $-43 \pm 65\text{‰}$ ,  $n=12$ ) than mid- and outer shelf stations (mean =  $-199 \pm 55\text{‰}$ ,  $n=22$ ; one-way ANOVA,  $P<0.01$ ). In March and July the  $\Delta^{14}\text{C}$ -DOC signature of inner shelf stations ranged from  $-111\text{‰}$  to  $-6\text{‰}$  while outer shelf stations were less variable, having  $\Delta^{14}\text{C}$ -DOC signatures between  $-281\text{‰}$  and  $-242\text{‰}$  (Figures 10A-B). During the October sampling, inner shelf stations of transects B and C had similar and relatively enriched  $\Delta^{14}\text{C}$ -DOC values ( $41\text{‰}$  to  $52\text{‰}$ ), although station D01 had a more depleted value ( $-110\text{‰}$ ; Figure 10C). Similar results were found at the outer shelf stations in October where  $\Delta^{14}\text{C}$ -DOC signatures were more enriched along transects B and C ( $-135\text{‰}$  to  $-133\text{‰}$ ) than on D transect ( $-248\text{‰}$ ; Figure 10C).

$\Delta^{14}\text{C}$  and  $\delta^{13}\text{C}$  values of POC (Table 4; Figures 11A-C and 12A-C) were much more variable than for DOC. There were no clear spatial patterns in POC isotopic composition in surface waters, most likely due to the heterogeneous nature of POC and its susceptibility to processes such as resuspension in shallow SAB shelf waters



(Nitrouer and Wright 1994). In surface waters,  $\delta^{13}\text{C}$ -POC ranged from -23.3‰ to -18.5‰ (Figures 11A-C), with these two extremes occurring at nearby stations during the March cruise. At inner shelf stations,  $\delta^{13}\text{C}$ -POC became significantly more depleted over the course of the year, averaging at  $-21.9 \pm 0.4\text{‰}$  in March (n=4) and  $-20.9 \pm 0.3\text{‰}$  in October (n=4; one-way ANOVA,  $P < 0.01$ ). Overall,  $\delta^{13}\text{C}$ -POC exhibited a relatively small range of values and variable spatial distributions.

The  $\Delta^{14}\text{C}$ -POC distributions allowed for some generalizations about spatial and temporal distributions to be identified (Figures 12A-C). In March, inner shelf  $\Delta^{14}\text{C}$ -POC tended to be more depleted (mean =  $-25 \pm 15\text{‰}$ , n=4), while mid- and outer shelf stations were overall more enriched with bomb- $^{14}\text{C}$  (mean =  $21 \pm 40\text{‰}$ , n=5; Figure 12A). In July and October, this distribution was reversed, where inner shelf POC tended to be more enriched in  $^{14}\text{C}$  than on the outer shelf (Figures 12B-C). In July,  $\Delta^{14}\text{C}$ -POC signatures on C transect ranged from 36‰ on the inner shelf to 12‰ on the outer shelf (Figure 12B).  $\Delta^{14}\text{C}$ -POC signatures in October were more depleted than in March and July, ranging from a high of -3‰ on the inner shelf (mean =  $-28 \pm 17\text{‰}$ , n=4) to a low of -91‰ on the outer shelf (mean =  $-66 \pm 33\text{‰}$ , n=4; Figure 12C). One striking feature of the October  $\Delta^{14}\text{C}$ -POC data was that on the mid shelf signatures were modern and bomb  $^{14}\text{C}$ -enriched, i.e., up to +2‰. The outer shelf stations displayed a significant seasonal change in the  $\Delta^{14}\text{C}$ -POC signature; in March outer shelf samples were enriched (mean =  $21 \pm 40\text{‰}$ , n=5) while in October they were more depleted (mean =  $-66 \pm 33\text{‰}$ , n=4; one-way ANOVA,  $P = 0.01$ ).

Deep outer shelf and slope waters (>~400 m) were collected on all cruises, and selected samples were analyzed for isotopic signatures in order to characterize the Gulf Stream as a potential end member (Table 4). DOC concentration was ~50  $\mu\text{M}$  in these deeper waters while POC concentration was <~6  $\mu\text{g/L}$  (Table 3). The  $\delta^{13}\text{C}$  of DOC averaged  $-22.0 \pm 0.6\text{‰}$  (n=4), while  $\Delta^{14}\text{C}$ -DOC averaged  $-379 \pm 16\text{‰}$  (n=4; Table 4).

The isotopic composition of Gulf Stream POC was also depleted, with  $\delta^{13}\text{C}$  averaging  $-26.6 \pm 2.0\text{‰}$  ( $n=3$ ), and  $\Delta^{14}\text{C}$  averaging  $-395 \pm 128\text{‰}$  ( $n=3$ ; Table 4).

### ***N and P Distributions in the SAB***

DON and DOP concentrations, which are the forms of the nutrient elements of greatest interest to the present study, are presented in Figures 13A-C, 14A-C, 15A-C, and 16A-C and Table 3. In addition, Appendix Table 1 lists all inorganic and organic nutrient data for all samples from the three 2005 SAB cruises (i.e.,  $\text{NH}_4^+$ ,  $\text{NO}_2^- + \text{NO}_3^-$ ,  $\text{PO}_4^-$ , TDN, TDP). Surface concentrations of DON in the inner SAB were ~2-3-fold higher than mid- and outer shelf stations (Table 3; Figures 13A-C and 14A-C). Typically, the largest decrease in DON occurred in surface waters between the inner- and mid shelf regions, while smaller decreases occurred between the mid- and outer shelves (Figures 13A-C). Concentrations of DON in surface waters during the March cruise showed the lowest range of values of all three cruises (2-8  $\mu\text{M}$ ; Figure 13A). In July and October 2005, surface concentrations of DON ranged from ~15  $\mu\text{M}$  on the inner shelf at station C01 to ~6  $\mu\text{M}$  at outer shelf stations (Figures 13B-C). Depth profiles in March show a doubling of DON concentrations at depths  $>\sim 100\text{m}$  at outer shelf stations, ranging from ~5  $\mu\text{M}$  in surface waters to ~9  $\mu\text{M}$  at depth (Figure 14A). However, in July and October, DON concentrations decreased or showed little change at depth (remaining at ~4  $\mu\text{M}$  at outer shelf stations; Figures 14B and C, respectively).

Throughout 2005, DOP concentrations in surface waters were consistently low ( $< \sim 0.3 \mu\text{M}$ ) making it difficult to identify any consistent spatial or temporal patterns using the present analytical method and limitations (Table 3; Figures 15A-C and 16A-C). DOP concentrations at depths  $>100 \text{ m}$  showed similar general distributions to the DON concentrations, where there was an increase in March (from  $<0.1 \mu\text{M}$  at the surface to ~0.7  $\mu\text{M}$  at depth; Figure 16A). However, in July and October, DOP either decreased or showed little change over the water column (Figures 16B-C). At depths  $> 100 \text{ m}$ , any P

present was usually entirely in the inorganic form, resulting in estimated DOP concentrations that were below detection (Figures 16A-C).

In March, there appeared to be anomalous distributions of DON and DOP in deeper waters (>100 m). DON in surface waters was relatively high (~8  $\mu\text{M}$ ) at inner shelf stations, and considerably lower (~2  $\mu\text{M}$ ) at the mid and outer shelf stations, especially along the northernmost transect (E; Figure 13A). E transect had the highest concentrations of DOP in surface waters in March (~0.2  $\mu\text{M}$ ; Figure 15A). Perhaps most intriguing, however, was during March in deep outer shelf waters (>150 m), when concentrations of DOC remained at background levels (~50  $\mu\text{M}$ ), there was a large concomitant increase in DON and DOP concentrations up to ~14  $\mu\text{M}$  and ~0.7  $\mu\text{M}$ , respectively (Table 3; Figures 14A and 16A).

#### ***Distributions and Isotopic Signatures of DIC in the SAB***

Concentrations of DIC in surface waters (<50 m water depth; Table 5; Figures 17A-C) were generally lower on the inner shelf (mean =  $2022 \pm 66 \mu\text{M}$ , n=30) of the SAB than the mid- and outer shelf regions (mean =  $2076 \pm 44 \mu\text{M}$ , n=80; t-test,  $P < 0.01$ ). The lowest concentrations of DIC were often found at station C01. Each sampling period had unique and differentiable surface distributions of DIC (Figures 17A-C). In March, an across-shelf gradient was observed, but in July and October, DIC concentrations had stronger north-south differences. Throughout the year, DIC concentrations also increased in deeper waters (>50 m) of the outer shelf region (Figures 18A-C).

In March 2005, DIC concentrations displayed an across-shelf distribution, with concentrations highest on the mid-shelf (2135  $\mu\text{M}$ ) and lowest on the inner shelf (2040  $\mu\text{M}$ ; Figure 17A). During the summer sampling period, in July, surface water samples had a smaller range of DIC concentrations (from 2000  $\mu\text{M}$  to 2120  $\mu\text{M}$ ; Figure 17B). At this time, there appeared to be a north-south gradient in DIC, where the highest concentrations were observed along B transect at the inner and mid shelf stations and

lower concentrations of DIC along C and D transects (Figure 17B). Surface water DIC from the October cruise (Figure 17C) was lowest along C transect (ranging from 1950  $\mu\text{M}$  at C01 to 2020  $\mu\text{M}$  at C15), while increasing up to 2170  $\mu\text{M}$  at outer shelf stations to both the north and south (Figure 17C).

Generally, the isotopic signatures of DIC in surface waters (upper  $\sim 2$  m) displayed an across-shelf increase in  $\delta^{13}\text{C}$ , but not in  $\Delta^{14}\text{C}$ .  $\delta^{13}\text{C}$ -DIC was depleted at inner shelf stations throughout the year, averaging  $-0.1 \pm 0.9\text{‰}$  ( $n=30$ ) in surface waters, and enriched at mid- and outer shelf stations, averaging  $1.1 \pm 0.4\text{‰}$  ( $n=80$ ; t-test,  $P<0.01$ ; Table 5; Figures 19A-C). At inner shelf stations,  $\delta^{13}\text{C}$ -DIC became significantly more depleted as the year progressed (Figures 19A-C), averaging  $0.1 \pm 0.5\text{‰}$  in March ( $n=10$ ) and  $-0.6 \pm 0.7\text{‰}$  ( $n=10$ ) in October (one-way ANOVA,  $P=0.03$ ). In outer shelf stations throughout 2005, there were slight significant shifts in  $\delta^{13}\text{C}$ -DIC signatures, resulting in decreases from a mean of  $1.2 \pm 0.4\text{‰}$  in the upper water column ( $<\sim 50$  m,  $n=33$ ) to a mean of  $0.8 \pm 0.2\text{‰}$  in deeper water ( $>\sim 50$  m,  $n=43$ ; t-test,  $P<0.01$ ; Figures 20A-C).  $\Delta^{14}\text{C}$ -DIC in the upper water column ( $<\sim 50$  m) ranged from 50‰ to 100‰ (Table 5; Figures 21A-C and 22A-C). Bomb- $^{14}\text{C}$  was evident in all waters  $<\sim 500$  m depth, and there was a dramatic decrease in  $\Delta^{14}\text{C}$ -DIC in deeper waters with values ranging from -74 to -33‰ (Figures 22A-C).

In addition, three samples of deep slope water ( $> \sim 900$  m) were collected and analyzed (one from each of the three cruises) to characterize the Gulf Stream component. These values were consistent between the three cruises, with DIC concentrations varying by  $\leq 25$   $\mu\text{M}$  (range of 2250 to 2275  $\mu\text{M}$ ) and the  $\delta^{13}\text{C}$ -DIC and  $\Delta^{14}\text{C}$ -DIC signatures averaging  $1.0 \pm 0\text{‰}$  and  $-32 \pm 5\text{‰}$  ( $n = 3$ ), respectively (Table 5).

### ***SAB Shelf DOM Dark Decomposition Experiments***

The DOM dark decomposition experiments were not always successful in that there were problems with contamination in several of the 20L containers, particularly in

the early parts of this study, resulting in increases in DOC concentration over time. As a consequence, these results are not included here. In the March 2005 incubations, all containers appeared to have been exposed to an unknown source of contamination after 180 days and no final samples were collected. Therefore, results from the first 152 days of the experiment only were used to calculate the DOC decay rate coefficients for March. For all other experiments, the full time series of the incubations was used to calculate DOC decay rate coefficients (Table 6).

The DOC decay rate coefficients were calculated from changes in DOC concentrations over the course of the experiments (Table 6; Figures 23A-C). In March the DOC decay rate coefficient ( $k$ ) on the inner shelf was  $0.00049 \text{ day}^{-1}$  ( $n=1$ ) and increased toward the outer shelf (mean  $k = 0.00118 \pm 0.00011 \text{ day}^{-1}$ ,  $n=2$ ; Table 6 and Figure 23A). This pattern was reversed in October, where higher decay rate coefficients were observed on the inner shelf (Table 6). The July incubation series showed relatively small and inconsistent changes in DOC concentration over the course of the experiment (Figures 23B and 24A), except at the inner shelf station where an average of  $22 \mu\text{M}$  of DOC was lost (mean  $k = 0.00033 \pm 0.00001 \text{ day}^{-1}$ ,  $n=2$ ; Table 6). The most dramatic changes of these experiments occurred in the October incubations (Figures 23C and 24C). Losses of DOC over 216 days averaged  $48 \mu\text{M}$  on the inner shelf (mean  $k = 0.00085 \pm 0 \text{ day}^{-1}$ ,  $n=2$ ), while the mid shelf lost an average of  $16 \mu\text{M}$  DOC (mean  $k = 0.00065 \pm 0 \text{ day}^{-1}$ ,  $n=2$ ) and the outer shelf gained an average of  $137 \pm 16 \mu\text{M}$  DOC ( $n=2$ ; Figures 23C and 24C).

Results from the final nutrient samples for the July and October incubations (Appendix Table 2 displays all nutrient concentrations measured) showed that ~40-70% of the initial DON was utilized (Table 6; Figures 24B and D), while only ~5-20% of the initial DOC was utilized (of experiments where there was a decrease in both replicates; Table 6; Figures 24A and C). In July, mid- and outer shelf stations utilized a slightly larger percentage of the DON (mean =  $68 \pm 6\%$ ,  $n=4$ ) than the inner shelf (mean =  $57 \pm$

0%, n=2; Table 6), although these mid- and outer shelf waters had smaller initial concentrations of DON, and net DOC decreases did not occur in those experiments (Figures 24A-B). In October, the mid-shelf incubation utilized the largest portion of DON, average ~67% (Table 6). Even in containers that experienced an increase in DOC, the DON concentration still decreased, such as the October outer shelf stations (Figures 24C-D).

Inner- and mid shelf incubations in October 2005 were considered the most successful as they had the lowest replicate errors and showed the largest DOC decrease; therefore, these samples were chosen for DOC isotopic analyses. Results from inner- and mid shelf waters showed minimal changes in  $\delta^{13}\text{C}$ -DOC (mean =  $0.9 \pm 0.8\text{‰}$ , n=4; Figure 25A). In contrast, there was a large and significant (t-test,  $P < 0.05$ ) decrease in  $\Delta^{14}\text{C}$ -DOC at both sites following decomposition (Figure 25B). The remaining, undegraded (i.e., refractory) DOC was more depleted in  $^{14}\text{C}$  than the starting material. Inner shelf DOC decreased by an average of  $-87 \pm 9\text{‰}$  (n=2; Figure 25B), while the mid shelf station had a larger shift, decreasing by an average of  $-167 \pm 20\text{‰}$  (n=2; Figure 25B).

### ***River and Salt Marsh End Members***

Increases in river discharge are likely to affect the physical and chemical properties of inner shelf stations, most notably salinity distributions. Relative to the median daily statistic (ranging between 6 and 60 years depending on the specific river), mean daily discharge during the period of this project tended to be above average in 2005 and below average in 2006 (Figures 5A-D). The 2005 spring peak in river discharge occurred later than normal, beginning during the March cruise, while in July 2005 there was an atypical peak in river discharge that was well above the median daily flow statistic (Figures 5A-D). Interestingly, this was not reflected in shelf salinity or nutrient anomalies, which showed the lowest variation during this time. Another peak in river

flow (Figures 5A-D) was evident during the October 2005 cruise, potentially increasing the export of terrestrial materials. During the end member sampling trip in July 2006, river discharge in the Altamaha and Savannah Rivers was lower than the median daily flow statistic (Figures 5A-D).

Sample sites for terrestrial sources are listed in Table 2, along with key physical parameters measured; results of nutrient analyses are contained in Appendix Table 3. Not all rivers sampled were analyzed for DOC and POC isotopic composition due to time and cost constraints. Based on location and discharge, the Altamaha, Savannah, and Great Pee Dee Rivers were chosen for OC isotopic characterization. In these rivers, both the DOC and POC isotopes were indicative of modern, terrestrial materials (Table 4). The  $\delta^{13}\text{C}$ -DOC averaged  $-28.3 \pm 0.2\text{‰}$  ( $n=3$ ), and the  $\Delta^{14}\text{C}$ -DOC averaged  $69 \pm 28\text{‰}$  ( $n=3$ ) for the three rivers. The isotopic composition of POC was similar at all riverine sites, with  $\delta^{13}\text{C}$  averaging  $-30.6 \pm 2.1\text{‰}$  ( $n=4$ ), and the  $\Delta^{14}\text{C}$  averaging  $-26 \pm 22\text{‰}$  ( $n=4$ ; Table 4).

$\delta^{13}\text{C}$ -DOC from salt marsh tidal creeks ranged from  $-22.7\text{‰}$  to  $-20.4\text{‰}$ , while  $\delta^{13}\text{C}$ -POC ranged from  $-24.7\text{‰}$  to  $-22.9\text{‰}$  (Table 4). Radiocarbon results from duplicate samples at the Sapelo River site indicated that both DOC and POC were modern and recently produced, with average values of  $16 \pm 26\text{‰}$  and  $-1 \pm 17\text{‰}$  ( $n = 2$ ), respectively (Table 4). The radiocarbon results from Hudson Creek were unusual in that both DOC and POC were relatively depleted in  $^{14}\text{C}$  compared to the other sites, resulting in  $\Delta^{14}\text{C}$  signatures of  $-38\text{‰}$  and  $-321\text{‰}$  ( $n = 1$ ), respectively (Table 4).

DIC concentrations in the salt marsh creeks sampled exceeded those of all other samples in this study ( $>2400 \mu\text{M}$ ), and had depleted  $\delta^{13}\text{C}$  signatures (mean =  $-3.3 \pm 0.4\text{‰}$ ;  $n=3$ ), and bomb-enriched  $\Delta^{14}\text{C}$  (mean =  $28 \pm 7\text{‰}$ ;  $n=3$ ; Table 5). River samples were more variable in DIC concentrations and isotopic compositions, but appeared to separate into two general groups based on salinity. The Savannah, Great Pee Dee, and Cape Fear Rivers had lower concentrations of DIC ( $<600 \mu\text{M}$ ), and were more depleted

in  $\delta^{13}\text{C}$  (ranging from -15‰ to -11‰) and  $\Delta^{14}\text{C}$  (ranging from -72‰ to -1‰; Table 5). The St. Johns, Altamaha, and Cooper Rivers had much greater concentrations of DIC ( $>1200\ \mu\text{M}$ ), were enriched  $\delta^{13}\text{C}$  (-5.1‰ to -2.4‰) and had a smaller range of depleted  $\Delta^{14}\text{C}$  signatures (ranging -70‰ to -37‰; Table 5). These groupings were not based on river type, i.e., piedmont and blackwater rivers, as initially expected, but instead may be related to the salinity of each particular sample, where salinity and estuarine mixing processes may have affected the DIC concentrations and isotopic compositions. The Savannah and Great Pee Dee Rivers were sampled in completely fresh water portions ( $S < 1$ ) and will be referred to as “fresh water rivers”, while the Cape Fear, Altamaha and St. Johns Rivers were moderately saline ( $S < 10$ ), and the Cooper River was estuarine ( $S \sim 25$ ) and will be referred to as “estuarine rivers” when referring to DIC parameters (Table 5).



## DISCUSSION

In the present study, elemental distributions and carbon isotope signatures were measured, and DOM dark decomposition experiments were conducted in the SAB during three periods in 2005. These characteristics are now examined as a function of both shelf region (i.e., across-shelf and along-shelf distributions) and time of year (i.e., across the three cruises) in an attempt to evaluate the sources and cycling of organic materials in the SAB.

Elemental stoichiometric relationships are used to identify sources of OM (terrestrial and marine; Meyers-Schulte and Hedges 1986; Hedges et al. 1997; Benner 2002) as well as to assess whether different components (i.e., DOC, DON, or DOP) are preferentially remineralized in the SAB as has been found in other systems (Hopkinson et al. 1997; Loh and Bauer 2000). Dual isotope mass balance models are also employed for DOC, POC and DIC to estimate the relative inputs of different carbon sources to the SAB for each of these major carbon pools (Raymond and Bauer 2001c; Bauer et al. 2002).

Relationships between various organic and isotopic parameters and salinity (i.e., to examine physical mixing vs. non-conservative behavior) are further examined through a number of regressions (Bauer et al. 2002; Wang et al. 2004). Correlation analyses are used to identify major temporal and regional differences between pairs of dependent DOM parameters. However, these correlative relationships were mainly confined to the DOM results, as the DOM pool was most extensively examined in this study, and because fewer parameters were measured for the POM and DIC pools.

These findings are compared to analogous OM and isotopic distributions and DOM decomposition findings for the adjacent Middle Atlantic Bight, the only other ocean margin where a similar type of large-scale study of this nature has been conducted. Finally, a conceptual model of the interactions between and cycling of organic and inorganic carbon components for the SAB is developed in an attempt to integrate the results and findings from this study.

## ***General Organic Matter and Isotopic Distributions in the SAB***

### Regional Variability

DOC concentrations were greatest in shallow surface waters (upper ~2 m), with surface maxima occurring inshore near the coastal salt marshes of GA (e.g., station C01) and decreasing sequentially at mid and outer shelf sites (Figures 6A-C). This is hereafter considered the “typical” across-shelf distribution. Surface DOC concentrations during this study ranged from a maximum on the inner shelf of 240  $\mu\text{M}$  in October to a background level of ~80  $\mu\text{M}$  in outer shelf waters (Figures 6A-C). A similar DOC concentration range (~275  $\mu\text{M}$  on the inner shelf and ~75  $\mu\text{M}$  on the mid shelf) and inner- to mid shelf decreases were previously reported for the SAB by Moran (1991). DOC across-shelf decreases in SAB surface waters were also similar to findings in the mid-1990s for the Mid Atlantic Bight (MAB), where surface concentrations were highest on the inner shelf (~150  $\mu\text{M}$ ) and decreased sequentially to ~50  $\mu\text{M}$  in outer shelf waters (Vlahos et al. 2002). However, it is important to note that the SAB had overall higher concentrations of DOC in surface waters than the MAB of both inner shelf stations (~100  $\mu\text{M}$  higher) and outer shelf stations (~25  $\mu\text{M}$  higher).

Surface POC concentrations in this study also had an inner shelf maximum of up to 698  $\mu\text{g/L}$  and decreased to a background level of ~20  $\mu\text{g/L}$  at outer shelf stations (Figures 8A-C). POC concentrations in the SAB reported by Griffith et al. (1990) were similar to results from this study for inner shelf stations (~1,000  $\mu\text{g/L}$ ), but higher at mid shelf stations (~100  $\mu\text{g/L}$ ). In the MAB, surface POC concentrations had generally lower concentrations but similar across-shelf decreases to the SAB. Similar to DOC, the MAB had a smaller range in POC (27 to 336  $\mu\text{g/L}$ ; Bauer et al. 2002) than the SAB (~20 to 698  $\mu\text{g/L}$ ).

DON concentrations in the SAB also showed across-shelf decreases (Figures 13A-C), while DOP concentrations were more spatially variable (Figures 15A-C). At outer shelf stations (A08, B11, C15, D11, and E11) and in deep waters (>~100 m), DOC,

DON and DOP generally decreased sharply (Figures 7A-C, 14A-C and 16A-C), as DIN and DIP increased (Appendix Table 1 and Appendix Figure 1), with the exception of certain sites in March 2005 which are discussed in detail below. These inner shelf maxima in DOC, POC, and DON concentrations suggest a source of DOM and POM to the SAB shelf at the land-ocean margin. The absence of these materials on the mid- and outer shelves further suggests that they were rapidly recycled on the inner shelf region (Yoder 1985).

Throughout 2005,  $\delta^{13}\text{C}$ -DOC in SAB surface waters tended to be significantly more depleted (one-way ANOVA,  $P < 0.01$ ; Figures 9A-C) at inner (mean =  $-24.0 \pm 0.7\text{‰}$ ,  $n=12$ ) compared to mid- and outer shelf stations (mean =  $-22.1 \pm 0.6\text{‰}$ ,  $n=22$ ), possibly suggesting a greater contribution of terrestrial  $\text{C}_3$  plant material in the nearshore zone. Significantly enriched  $\Delta^{14}\text{C}$ -DOC signatures (one-way ANOVA,  $P < 0.01$ ; Figures 10A-C) at inner shelf stations (mean =  $-43 \pm 65\text{‰}$ ,  $n=12$ ) compared to mid- and outer shelf stations (mean =  $-199 \pm 55\text{‰}$ ,  $n=22$ ), further suggest that younger, more recently produced sources of OM dominate the DOC pool closer to land.  $\delta^{13}\text{C}$ -DOC in surface samples had a slightly larger range in the SAB ( $-24.8\text{‰}$  to  $-21.0\text{‰}$ ; Figures 9A-C) than the MAB ( $-23.7\text{‰}$  to  $-21.8\text{‰}$ ; Bauer et al. 2002), possibly indicating a greater range in the relative contributions of terrestrial vs. marine DOM to the entire SAB on an annual basis.  $\Delta^{14}\text{C}$ -DOC tended to be more enriched, or “younger” in the SAB ( $-281\text{‰}$  to  $54\text{‰}$ ; Figures 10A-C) than the MAB ( $-306\text{‰}$  to  $-29\text{‰}$ ; Bauer et al. 2002), indicating either that sources of DOC to the SAB are dominated by younger average material than the MAB, or that DOC cycling in these two margins occurs on different time scales.

In contrast to DOC, POC isotopic signatures were much more variable both regionally and throughout 2005, and did not show any clear spatial across-shelf changes in surface waters during this study (Figures 11A-C and 12A-C). In surface waters of the SAB,  $\delta^{13}\text{C}$ -POC values ranged from  $-23.3\text{‰}$  to  $-18.5\text{‰}$  (Table 4; Figures 11A-C) and  $\Delta^{14}\text{C}$ -POC values ranged from  $-109\text{‰}$  to  $61\text{‰}$  (Table 4; Figures 12A-C). Relatively

similar ranges were found in MAB upper water column, however,  $\delta^{13}\text{C}$ -POC values there were somewhat lower, ranging from -24.8‰ to -19.9‰, and  $\Delta^{14}\text{C}$ -POC values were somewhat elevated -68‰ to 78‰ (Bauer et al. 2002) compared to the SAB. These results indicate that POC was not comprised of completely modern material derived from shelf primary production in either region (Bauer et al. 2002), but rather consisted of significant amounts of aged, presumably refractory, material having significant terrestrial  $\delta^{13}\text{C}$  character.

Relative to the “typical” across-shelf OM distributions, DIC concentrations showed a reverse across-shelf distribution for all sample periods in 2005, where the lowest concentrations typically occurred on the inner shelf (mean =  $2006 \pm 61 \mu\text{M}$ ,  $n=21$ ) and increased towards the outer shelf ( $< \sim 50$  m, mean =  $2073 \pm 35 \mu\text{M}$ ,  $n=33$ ; Figures 17A-C). As expected, DIC also increased with depth ( $> \sim 50$  m, mean =  $2222 \pm 48 \mu\text{M}$ ,  $n=43$ ; Figures 18A-C) at all stations where deeper samples were collected. This across-shelf increase and shelf DIC concentrations ( $\sim 1900$  to  $2100 \mu\text{M}$ ) are consistent with results previously reported by Cai et al. (2003) and Wang et al. (2005) for surveys conducted in the SAB (in 2000 and 2002). In the MAB, DIC concentrations were generally similar to those in the SAB, ranging from  $1847 \mu\text{M}$  to  $2113 \mu\text{M}$  in the upper water column ( $< \sim 50$  m; Bauer et al. 2002).

Throughout the year,  $\delta^{13}\text{C}$ -DIC values in the upper water column ( $< \sim 50$  m) were significantly depleted (t-test,  $P < 0.01$ ; Figures 19A-C and 20A-C) at inner shelf stations (mean =  $-0.1 \pm 0.9\text{‰}$ ,  $n=30$ ) than at mid- and outer shelf stations where the isotopic signature was more enriched (mean =  $1.1 \pm 0.4\text{‰}$ ,  $n=80$ ). These  $\delta^{13}\text{C}$ -DIC signatures suggest the importance of river and terrestrial sources of DIC, fueled by heterotrophic processes in rivers, estuaries and/or on the inner shelf. Conversely, autotrophic processes on the mid- and outer shelf likely dominate the enriched  $\delta^{13}\text{C}$ -DIC signature there (Spiker 1980; Coffin et al. 1994). In MAB shelf waters,  $\delta^{13}\text{C}$ - ranged from 0.0 to 2.0‰ (Bauer et al. 2002), suggesting a possible greater prevalence of autotrophic conditions in the MAB

compared to the SAB (Spiker 1980; Coffin et al. 1994).  $\Delta^{14}\text{C}$ -DIC was similarly enriched throughout surface waters in both the SAB (<~50 m; 48‰ to 94‰; Figures 21A-C) and MAB (<~100 m; 31 to 80‰; Bauer et al. 2002) indicating the dominance of modern sources of DIC from a combination of OM respiration and air-sea exchange along the entire US east coast ocean margin.

In deep waters (>~500 m) of the outer shelf/slope of the SAB, DIC concentrations increased (mean =  $2251 \pm 26 \mu\text{M}$ ,  $n=17$ ; Figures 18A-C), and both  $\delta^{13}\text{C}$ -DIC (mean =  $0.8 \pm 0.2\text{‰}$ ,  $n=17$ ; Figures 20A-C) and  $\Delta^{14}\text{C}$ -DIC signatures (mean =  $-40 \pm 28\text{‰}$ ,  $n=9$ ; Figures 22A-C) decreased, suggesting the presence of deeper, older Gulf Stream waters (Severinghaus et al. 1996). DIC in deeper waters (>~300 m) of the MAB had a similar increase in concentration (up to  $2205 \mu\text{M}$ ), while  $\delta^{13}\text{C}$ -DIC had a similar range as surface waters (0.6 to 1.2‰) and  $\Delta^{14}\text{C}$ -DIC was depleted (-51 to 5‰; Bauer et al. 2002).

### Temporal Variability

For the majority of the year, net alongshore SAB water circulation is typically south to north (Lee et al. 1991; Menzel 1993). Mean circulation in the nearshore region reverses in the fall (i.e., October) due to changes in wind direction, resulting in a net southward alongshore water flow (Lee et al. 1991). This change in nearshore mean flow direction was evident in surface distributions of several of the chemical parameters during the October 2005 cruise. Specifically, the inner shelf of B transect (station B01) had very similar concentrations of DOC, DON and DOP and DOC isotopic compositions as the inner shelf maxima of C transect (station C01; Figures 6C, 9C, 10C, 13C, and 15C). This suggests that terrestrial DOM was being transported southward during this time period, potentially affecting inner shelf nutrient recycling processes and the composition of materials exported across the SAB shelf to the ocean (Lee et al. 1991).

OM concentrations remained relatively constant throughout the year in mid- and outer shelf surface waters (~2 m; DOC mean =  $86 \pm 14 \mu\text{M}$ ,  $n=63$ ; DON mean =  $5.8 \pm$

1.5  $\mu\text{M}$ ,  $n=66$ , POC mean =  $55 \pm 37 \mu\text{g/L}$ ,  $n=17$ ). However, temporal increases were noted for DOC (Figures 6A-C), DON (Figures 13A-C) and POC (Figures 8A-C) in surface waters ( $\sim 2$  m) of inner shelf stations from March to October 2005. Surface water DOC for inner shelf stations increased from a mean of  $130 \pm 24 \mu\text{M}$  ( $n=9$ ) in March 2005 (Figure 6A) to  $170 \pm 45 \mu\text{M}$  ( $n=10$ ) in October (Figure 6C); concomitantly, DON increased in surface waters of inner shelf stations from a mean of  $6.7 \pm 0.9 \mu\text{M}$  ( $n=12$ ) in March (Figure 13A) to a mean of  $11.0 \pm 1.9 \mu\text{M}$  ( $n=10$ ) in October (Figure 13C). Inner shelf surface water POC concentrations also increased throughout the year, particularly at station C01, with lower concentrations in March ( $208 \mu\text{g/L}$ ; Figure 8A) and the highest in October ( $698 \mu\text{g/L}$ ; Figure 8C). These findings suggest that the magnitude of terrestrial DOM and POM sources increased as the year progressed. However, the increases in DOM and POM throughout 2005 in the nearshore SAB were not directly related to river runoff (Figures 5A-D). By comparison, temporal variations in DOM and POM in the MAB were notably different from the SAB in that DOC concentrations varied little ( $\sim 5$  to  $10 \mu\text{M}$ ; Bauer et al. 2002; Vlahos et al. 2002), and POC concentrations were higher in March than August 1996 (Bauer et al. 2002), presumably due to the well-established spring phytoplankton bloom in the MAB.

Few significant temporal changes were found in the DOC isotopic composition at inner- and outer shelf stations (Figures 9A-C and 10A-C). Mean  $\delta^{13}\text{C}$ -DOC was  $-24.0 \pm 0.7\text{‰}$  ( $n=12$ ) at inner shelf stations and  $-22.1 \pm 0.6\text{‰}$  ( $n=22$ ) at mid- and outer shelf stations (Figures 9A-C), suggesting that sources of DOC to these regions of the SAB did not change over 2005. In contrast,  $\Delta^{14}\text{C}$ -DOC exhibited seasonal enrichment from March to October 2005 (Figures 10A-C). At inner shelf stations,  $\Delta^{14}\text{C}$ -DOC increased from a mean of  $-72 \pm 33\text{‰}$  ( $n=6$ ) in March (Figure 10A) to a mean of  $-15 \pm 87\text{‰}$  ( $n=5$ ) in October (Figure 10C) suggesting that in the spring, when river discharge to the SAB was highest (Figures 5A-D) older DOC was exported to the shelf. At mid- and outer shelf stations,  $\Delta^{14}\text{C}$ -DOC also increased significantly (one-way ANOVA,  $P < 0.01$ ) from a mean

of  $-222 \pm 33\text{‰}$  (n=12) in March (Figure 10A) up to a mean of  $-150 \pm 61\text{‰}$  (n=7) in October (Figure 10C), possibly suggesting an accumulation of young, phytoplankton derived material further out on the SAB shelf in summer and fall. Similar temporal variations in carbon isotopic signatures were found for the MAB shelf, where  $\delta^{13}\text{C}$ -DOC signatures showed little temporal changes, but  $\Delta^{14}\text{C}$ -DOC signatures increased from March to August 1996 (Bauer et al. 2002).

Inner shelf station exhibited significant temporal changes in  $\delta^{13}\text{C}$ -POC and  $\Delta^{14}\text{C}$ -POC signature (Figures 11A-C and 12A-C).  $\delta^{13}\text{C}$ -POC at inner shelf stations became significantly enriched (one-way ANOVA,  $P < 0.01$ ) as the year progressed, from a mean of  $-21.9 \pm 0.4\text{‰}$  (n=4) in March 2005 (Figure 11A) to a mean of  $-20.9 \pm 0.3\text{‰}$  (n=4) in October 2005 (Figure 11C). In contrast, at outer shelf stations  $\delta^{13}\text{C}$ -POC became more depleted from March (mean =  $-20.4 \pm 1.9\text{‰}$ ; n=5; Figure 11A) to October (mean =  $-21.6 \pm 0.3\text{‰}$ ; n=4; Figure 11C).  $\Delta^{14}\text{C}$ -POC signatures showed little change at inner shelf stations throughout 2005, with a mean of  $-14 \pm 30\text{‰}$  (n=10; Figures 12A-C). Outer shelf stations exhibited a significant temporal decrease in  $\Delta^{14}\text{C}$ -POC signatures (one-way ANOVA,  $P = 0.01$ ); in March,  $\Delta^{14}\text{C}$ -POC was enriched (mean =  $21 \pm 40\text{‰}$ , n=5; Figure 12A), while in October, samples were  $^{14}\text{C}$ -depleted (mean =  $-66 \pm 33\text{‰}$ ,  $P = 0.01$ ; Figure 12C). These findings indicate that while inner shelf source POC age was not changing during the year, the age of POC on the outer shelf region decreased, possibly due to a relative loss of younger forms of POC (e.g., from primary production), or relative increases in older forms of POC (e.g., from sediment resuspension, or preferential utilization of the younger POC components).

This study found no significant temporal variations in concentrations of DIC at inner shelf stations (ranging from 1834 to 2140  $\mu\text{M}$ ; Table 5; Figures 17A-C and 18A-C). This is consistent with previous studies by Cai et al. (2003) and Wang et al. (2005) which also found no seasonal temporal increase in DIC concentrations on the SAB shelf. In contrast to the previous studies which found no significant changes at outer shelf stations

throughout the year (Wang et al. 2005), in the present study upper water column (<~50 m), outer shelf stations showed decreases in DIC as the year progressed, from a mean of  $2086 \pm 26 \mu\text{M}$  (n=8) in March, to a mean of  $2052 \pm 35 \mu\text{M}$  (n=6) in July, and  $2038 \pm 29 \mu\text{M}$  (n=6) in October (Figures 17A-C and 18A-C). These contrasting findings between the different studies may be a result of the earlier studies focusing exclusively on central C transect (Figure 4), whereas this study included results from three transects (B, C, and D). In addition, there are several possible physical and biological explanations for these temporal decreases at outer shelf stations, such as temperature and solubility effects as well as the balance between auto- and heterotrophic processes (Rau et al. 1992).

The isotopic composition of DIC in shelf surface waters (<~50 m) exhibited changes in  $\delta^{13}\text{C}$  signatures between the sampling periods, but little change in  $\Delta^{14}\text{C}$  was observed in these data (Table 5). At inner shelf stations,  $\delta^{13}\text{C}$ -DIC became significantly more depleted as the year progressed (one-way ANOVA,  $P=0.03$ ), from a mean of  $0.1 \pm 0.5\text{‰}$  (n=9) in March (Figure 19A) to a mean of  $-0.6 \pm 0.7\text{‰}$  (n=8) in October 2005 (Table 5; Figure 19C). However, in July, DIC signatures at the inner shelf station were most depleted with a mean of  $-1.3 \pm 0.9\text{‰}$  (n=4; Table 5; Figure 19B). These changes in  $\delta^{13}\text{C}$ -DIC signatures suggest a relative increase in heterotrophic processes (i.e., greater respiration of  $^{13}\text{C}$ -depleted OM) in July and October at inner shelf stations (Spiker 1980; Coffin et al. 1994). At outer shelf stations,  $\delta^{13}\text{C}$ -DIC signatures in surface waters (<~50 m) were more depleted in March (mean =  $1.2 \pm 0.2\text{‰}$ , n=8) than in July (mean =  $1.7 \pm 0.1\text{‰}$ , n=6) and October 2005 (mean =  $1.5 \pm 0.1\text{‰}$ , n=6; Table 5; Figures 19A-C), suggesting possible relative increases in either autotrophic processes or atmospheric exchange at outer shelf stations in the summer and fall (Spiker 1980; Coffin et al. 1994). Throughout 2005,  $\Delta^{14}\text{C}$ -DIC was enriched in surface waters (<~50 m), ranging from 48 to 94‰ in all regions of the SAB (Figures 21A-C) indicating the presence of modern DIC throughout the region.



These general spatial and temporal distributions are explored in greater detail below by comparing surface distributions to potential end member sources and by using isotope mass balance models to estimate the relative contributions of different sources to the major carbon pools in different parts of the SAB and at different times of the year.

### *Elemental Ratios of DOM*

Elemental stoichiometry may integrate the relative concentrations of different OM constituents (e.g., DOC, DON, and DOP) to reveal subtle changes in regional or temporal biogeochemical features such the production or preferential remineralization of different elements comprising the OM (Jackson and Williams 1985; Hopkinson et al. 1997). The relationships between DOC, DON, and DOP concentrations exhibited significant variability across this study (Figures 26A-C), however, an important general feature of nearly all samples in this study is that they fell significantly above Redfield ratios (i.e., C:N = 6.6, C:P = 106, and N:P = 16), with the exception of several outer shelf deep water stations in March 2005. Generally, DOC:DON deviated from Redfield in that samples were depleted in N relative to C (Figure 26A). Similarly, DOC:DOP and DON:DOP relationships deviated from Redfield where samples were depleted in P relative to C and N, respectively (Figures 26B and C). These relationships suggest preferential remineralization of DON and DOP relative to DOC in the SAB as a whole. Consequently, we would predict that relatively more DOC than DON and DOP is exported to the ocean from the SAB region (Hopkinson and Vallino 2005), and that more organic N and P is recycled on the SAB. Similar elemental relationships for DOM have been reported in the MAB (Hopkinson et al. 1997; Hopkinson and Vallino 2005) as well as in open ocean waters (Loh and Bauer 2000).

As noted above, there are several samples which fell below the Redfield ratio lines, all of which were collected from deep (>150 m) outer shelf/slope stations (D11 and E12) in March 2005 (Table 3; Figures 26A-C). These samples had relatively high DON

and DOP concentrations (up to  $\sim 14 \mu\text{M}$  and  $0.7 \mu\text{M}$ , respectively) relative to their DOC concentrations ( $\sim 50$  to  $75 \mu\text{M}$ ; Table 3), suggesting a possible decoupling of production/consumption processes at this time in these regions of the SAB. Elemental ratios including DOP are not discussed further here as their very low concentrations (frequently below detection) resulted in artificially high elemental ratios that were impossible to interpret (Appendix Table 1 lists DOC:DOP and DON:DOP ratios for stations where they are  $>0$ ).

Surface distributions of DOC:DON (Figures 27A-C) displayed subtle regional and temporal differences that were not obvious in the depth profiles (Figures 28A-C). In surface waters, DOC:DON ranged from  $\sim 11$  to  $34$  (Table 3 and Figures 27A-C), while in deep waters it had a much larger range from  $\sim 4$  to  $45$  (Table 3 and Figures 28A-C), indicating the greater relative inputs of N-rich material to surface waters, and remineralization of DON relative to DOC in deep waters. Throughout 2005, surface water DOC:DON was higher at the inner shelf of C transect, ranging from  $\sim 15$  to  $22$  (Figures 27A-C), and was likely indicative of terrestrial OM inputs such as vascular plant debris (Hedges et al. 1997). In surface waters at mid- and outer shelf stations, DOC:DON decreased to  $\sim 10$  (Figures 27A-C) suggesting that marine phytoplankton became a relatively more important influence on stoichiometry in these regions of the SAB (Hedges et al. 1997; Hopkinson et al. 1997).

In March 2005, surface distributions of DOC, DON, and DOP followed the typical across-shelf pattern (Figures 6A, 13A, and 15A, respectively), but the relative across-shelf change for each differed, resulting in higher DOC:DON ratios ( $>\sim 20$ ) at inner shelf stations than at mid and outer shelf stations (Figure 27A). A large anomaly in surface DOC:DON ratios occurred at station E07 (Figure 27A), where the ratio increased up to  $\sim 34$  due to unusually low DON concentrations ( $\sim 2 \mu\text{M}$ ; Figure 13A). During the July 2005 cruise, DOC:DON ratios in all surface water samples ranged from  $\sim 11$  on the inner shelf of A and B transects up to  $\sim 18$  at station E11, and displayed a south-north

rather than an across-shelf gradient (Figure 27B). October 2005 DOC:DON ratios in surface water samples showed relatively high DOC:DON values all along C transect in October, as well as extending along the inner shelf region (Figure 27C). In surface waters of the outer shelf stations, excluding C transect, the DOC:DON ratio decreased below 15, potentially indicating a shift towards phytoplankton dominating the DOM.

### ***DOC Sources and Behavior in the SAB***

#### **DOC-Salinity Mixing Relationships**

Mixing relationships between fresh water and marine end members may provide insights as to the conservative or non-conservative behavior of solutes, and may elucidate net sources or sinks along a salinity gradient in a system. These relationships were used in this study to assess potential DOC inputs and sinks throughout the SAB. DOC concentration,  $\delta^{13}\text{C}$ -DOC and  $\Delta^{14}\text{C}$ -DOC of SAB surface samples and potential end members were plotted as a function of salinity along with the calculated conservative distributions based on mixing between riverine and marine end members (Figures 29A-C). While DOC concentrations were highest in rivers (mean =  $608 \pm 427 \mu\text{M}$ ,  $n=3$ ) and salt marsh creeks (mean =  $713 \pm 303 \mu\text{M}$ ,  $n=2$ ; Figure 29A), riverine DOC was chosen as the end member for conservative mixing since this source represented a larger volume and could entrain salt marsh material en route (i.e., acting as an internal source) to the shelf region. The marine end member was represented by high salinity outer shelf surface water samples.

Surface shelf water DOC, which was limited to the upper portion of the salinity range ( $S > \sim 28$ ), appeared to mix relatively conservatively as the linear regression line for all surface samples (red dotted line) closely follows the conservative mixing line (solid black line; Figure 29A). This suggests that on the timescales relevant to mixing of river, estuarine and shelf waters, physical processes were mainly responsible for the across-shelf DOC concentration gradient and that any sources or sinks of DOC were acting at

similar magnitudes in the SAB. Moran et al. (1991) used lignin phenols as a tracer of terrestrial DOC in the inner shelf of the SAB and found that the behavior of these compounds was also largely conservative within the residence time of water on the shelf (~1-2 months). However, DOC concentrations alone may not be a sensitive index for determining net source/sink dynamics.

The distribution of DOC isotopes vs. salinity, again using SAB river waters as the low-salinity end-member (Figures 29B-C), suggests that DOC (or specific components of DOC) may have behaved less conservatively than suggested by the DOC concentration-salinity relationship (Figure 29A). At lower salinity stations ( $S < \sim 32$ ),  $\delta^{13}\text{C}$ -DOC signatures were heavier than predicted by the conservative mixing curve (solid black line; Figure 29B); this is evident in the deviation between the linear regression line for all surface samples (red dotted line) and the conservative mixing line (black solid line; Figure 29B). This deviation suggests the potential influence of isotopically heavier salt marsh creek OM on inner shelf  $\delta^{13}\text{C}$ -DOC (Figure 29B). At the higher salinity stations ( $S > \sim 32$ ) of the mid- and outer shelf region,  $\delta^{13}\text{C}$ -DOC generally followed the predicted mixing curve (black solid line) as seen by the linear regression line (red dotted line) nearing the conservative mixing line (black solid line; Figure 29B).

Similar features were observed for  $\Delta^{14}\text{C}$ -DOC vs. salinity (Figure 29C) for SAB surface waters, where  $\Delta^{14}\text{C}$ -DOC was enriched at lower salinity inner shelf stations ( $S < \sim 32$ ) and the linear regression line (red dotted line) deviates from the conservative mixing curve (black solid line; Figure 29C). At higher salinity stations, the linear regression line (red dotted line) more closely follows the conservative mixing line (black solid line; Figure 29C). Again, the salt marsh source, which was enriched in  $\Delta^{14}\text{C}$ , is speculated to be the source of the elevated  $\Delta^{14}\text{C}$ -DOC in the inner shelf region. March samples appeared to follow the  $\Delta^{14}\text{C}$ -DOC conservative distributions to a greater degree than July and October samples (Figure 29C) suggesting an increase in the  $\Delta^{14}\text{C}$ -DOC isotopic composition of terrestrial sources was changing as the year progressed.

### Relationships Between DOC Properties

Surface  $\delta^{13}\text{C}$ -DOC and  $\Delta^{14}\text{C}$ -DOC signatures were examined as a function of the corresponding DOC concentrations for each cruise period (Figures 30A and B, respectively). Lower concentrations of DOC ( $<\sim 100\ \mu\text{M}$ ) were observed from mid- and outer shelf stations, while higher DOC concentrations ( $>\sim 100\ \mu\text{M}$ ) occurred at inner shelf stations (Table 3). For all three sampling times in 2005, negative relationships were evident for  $\delta^{13}\text{C}$ -DOC vs. DOC concentration (Figure 30A). At higher DOC concentrations, the  $\delta^{13}\text{C}$ -DOC signature was more depleted, suggestive of a terrestrial DOC source, while enriched  $\delta^{13}\text{C}$ -DOC at correspondingly lower DOC concentrations ( $<\sim 100\ \mu\text{M}$ ) is indicative of greater contributions from a marine source of DOC (Fry and Sherr 1984; Michener and Schell 1994). The slopes of the correlation lines ( $\pm$  standard error) increased from March ( $-0.031 \pm 0.004$ ) to October ( $-0.016 \pm 0.004$ ; Figure 30A), due to the disproportionate increase in DOC concentration from March to October at inner shelf stations versus outer shelf stations. Y-intercepts of the lines ( $\pm$  standard error) ranged from  $-21.1 \pm 0.7$  in July to  $-19.8 \pm 0.4$  in March (Figure 30A) suggesting that there was little temporal variability in the low-concentration marine end-member  $\delta^{13}\text{C}$ -DOC signature over time. The decreases in slopes and relatively small changes in y-intercepts between sample periods suggest that while DOC concentrations were increasing throughout the year, source  $\delta^{13}\text{C}$ -DOC signatures were relatively invariant throughout the SAB over the course of this study.

In contrast to the negative correlation of  $\delta^{13}\text{C}$ -DOC vs. DOC concentration, a positive correlation was observed between  $\Delta^{14}\text{C}$ -DOC and DOC concentration for all sample periods (Figure 30B). At higher DOC concentrations ( $>\sim 100\ \mu\text{M}$ ), the  $\Delta^{14}\text{C}$ -DOC signatures were enriched indicating “younger” DOC was present on the inner shelf (Figure 30B), while at lower concentrations ( $<\sim 100\ \mu\text{M}$ ) in the mid- and outer shelf regions,  $\Delta^{14}\text{C}$ -DOC was depleted indicating a relative dominance of “older” DOC. This

may also be viewed as a relative absence of  $^{14}\text{C}$ -enriched DOC in mid and outer shelf waters. The slope of the correlation line ( $\pm$  standard error) for  $\Delta^{14}\text{C}$ -DOC vs. DOC concentration decreased from a high of  $2.1 \pm 0.2$  in March to  $1.5 \pm 0.3$  in both July and October (Figure 30B). This, combined with the offsets in the y-intercepts for the different months, suggests that there was a generally greater enrichment in for  $\Delta^{14}\text{C}$ -DOC in October than the other two sample periods. The greater slope in March indicates that there was a more rapid change in the  $\Delta^{14}\text{C}$ -DOC signature over a smaller range of DOC concentrations, whereas in July and October relatively proportional changes occurred between these parameters (Figure 30B).

Increases in the y-intercepts ( $\pm$  standard error) of the correlation lines from March ( $-384.6 \pm 22.6$ ) to July ( $-351.4 \pm 29.1$ ) to October ( $-286.2 \pm 38$ ; Figure 30B) suggest that the marine  $\Delta^{14}\text{C}$ -DOC end-member signature became more enriched (i.e., became younger) as the year progressed. These temporal changes in slopes and y-intercepts correspond with previously shown significant temporal increases from March to October in  $\Delta^{14}\text{C}$ -DOC at inner shelf and mid- and outer shelf stations and illustrate the temporal whole shelf increases in  $\Delta^{14}\text{C}$ -DOC which occurred between March and October 2005.

Surface DOC:DON ratios were also examined as a function of the corresponding  $\delta^{13}\text{C}$ -DOC and  $\Delta^{14}\text{C}$ -DOC signatures for each cruise period (Figures 31A-B) in order to further evaluate temporal changes in sources and characteristics of OM in the SAB. Throughout 2005, a negative relationship was observed in DOC:DON vs.  $\delta^{13}\text{C}$ -DOC (Figure 31A). Stations with depleted  $\delta^{13}\text{C}$ -DOC signatures had relatively higher DOC:DON ratios, suggesting that the DOM at these stations had greater terrestrial character than more offshore waters (Meyers-Schulte and Hedges 1986; Hedges et al. 1997). Conversely, stations with enriched  $\delta^{13}\text{C}$ -DOC signatures had relatively lower DOC:DON ratios suggesting a greater marine influence on the bulk DOM pool (Hedges et al. 1997; Benner 2002). DOC:DON was notably elevated in March compared to July and October ratios, suggesting either a more N-enriched form of terrestrial/riverine DOM

than expected, or greater contributions from shelf production in July and October 2005. The slope of the correlation lines ( $\pm$  standard error) for DOC:DON vs.  $\delta^{13}\text{C}$ -DOC increased from March ( $-1.740 \pm 0.696$ ) to October ( $-0.090 \pm 0.410$ ; Figure 31A) indicating that proportionally larger changes in DOC:DON ratios as a function of  $\delta^{13}\text{C}$ -DOC occurred in March than in July and October. The y-intercepts ( $\pm$  standard error) of these lines range from a low of  $-21.5 \pm 15.8$  in March, to a high of  $-1.0 \pm 6.3$  in July and an intermediate value of  $-5.7 \pm 9.2$  in October (Figure 31A) further supporting the idea that the SAB had a much stronger terrestrial/riverine DOM signal in March. These ranges of slopes and y-intercepts further illustrate the temporal changes in DOM composition in the SAB (Figure 31A) which was not evident in the  $\delta^{13}\text{C}$ -DOC signatures alone (Figures 9A-C) due to their relatively low dynamic range. In March terrestrial materials with higher DOC:DON ratios dominated the shelf, while in July and October, the terrestrial signal was mixed with another source, most likely of marine origin.

In contrast to the negative correlation for DOC:DON vs.  $\delta^{13}\text{C}$ -DOC, DOC:DON vs.  $\Delta^{14}\text{C}$ -DOC was positively correlated (Figure 31B), reflecting the contributions and admixing of younger, N-depleted terrestrial DOM with older but N-enriched marine DOM across the SAB. In comparison, stations with depleted  $\Delta^{14}\text{C}$ -DOC signatures had relatively lower DOC:DON ratios (Figure 31B). Similar to the DOC:DON vs.  $\delta^{13}\text{C}$ -DOC relationship (Figure 31A), the DOC:DON vs.  $\Delta^{14}\text{C}$ -DOC relationships are dominated by the more highly N-depleted March DOM, leading to a greater DOC:DON riverine end-member contribution (i.e., y-intercept) and a concomitant more depleted range  $\Delta^{14}\text{C}$ -DOC during this time. Overall, these differences in slopes and y-intercepts for DOC:DON vs.  $\Delta^{14}\text{C}$ -DOC again illustrate the dominance of relatively more highly aged, N-poor terrestrial materials in the DOM pool during March, than in July and October.

$\Delta^{14}\text{C}$ -DOC vs.  $\delta^{13}\text{C}$ -DOC for all SAB surface samples in 2005 (Figure 32A) were negatively correlated. Inner shelf stations were characterized by depleted  $\delta^{13}\text{C}$ -DOC (mean =  $-24.0 \pm 0.7\text{‰}$ , n=12) and enriched  $\Delta^{14}\text{C}$ -DOC (mean =  $-43 \pm 65\text{‰}$ , n=12), while

mid- and outer shelf stations were enriched in  $\delta^{13}\text{C}$ -DOC (mean =  $-22.1 \pm 0.6\text{‰}$ ,  $n=22$ ) and depleted in  $\Delta^{14}\text{C}$ -DOC (mean =  $-199 \pm 55\text{‰}$ ,  $n=22$ ; Figure 32A). These differences between inner shelf stations and mid- and outer shelf station isotopic compositions ( $\delta^{13}\text{C}$ -DOC and  $\Delta^{14}\text{C}$ -DOC) were statistically different for all 2005 samples (one-way ANOVA,  $P<0.01$ ). These findings are further evidence for the presence of significant amounts of terrestrial DOC, characterized by depleted  $\delta^{13}\text{C}$ -DOC and enriched  $\Delta^{14}\text{C}$ -DOC at inner shelf stations and a shift to greater relative amounts of marine DOC at mid- and outer shelf sites, characterized by more enriched  $\delta^{13}\text{C}$  and depleted or “older”  $\Delta^{14}\text{C}$ -DOC. It also appears that the mixing of isotopically unique DOM is relatively constant across shelf regions, as evidenced by the near-continuous relationship between  $\Delta^{14}\text{C}$ -DOC and  $\delta^{13}\text{C}$ -DOC. While  $\delta^{13}\text{C}$ -DOC appeared to have a similar range for each of the three cruises in this study, temporal changes in the  $\Delta^{14}\text{C}$ -DOC were apparent (Figure 32A). March and July DOC samples had a more depleted  $\Delta^{14}\text{C}$  signature (mean =  $-174 \pm 83\text{‰}$ ,  $n=22$ ) than the October samples which were relatively more enriched in  $\Delta^{14}\text{C}$  (mean =  $-94 \pm 98\text{‰}$ ,  $n=12$ ), suggesting that shelf DOC originated from a more modern source in Fall 2005.

#### DOC Isotopic Mass Balances

The  $\Delta^{14}\text{C}$ -DOC vs.  $\delta^{13}\text{C}$ -DOC relationship was further evaluated in relation to potential sources of DOC to the SAB (Figure 32B) using a dual isotope mass balance modeling approach. Potential sources of DOC to SAB surface waters include autochthonous microalgal production (in the water column), Gulf Stream intrusions, and terrestrial sources (both riverine and salt marsh exports). While the latter end members were measured directly, the isotopic composition of autochthonous SAB microalgal OC was estimated from the DIC isotopic composition of surface waters ( $<50$  m; Table 5) correcting for a  $-19\text{‰}$  fractionation (Bauer et al. 2001; Bauer et al. 2002), and resulting in a mean  $\delta^{13}\text{C}$  of  $-18.2 \pm 0.8\text{‰}$  ( $n=113$ ) and a mean  $\Delta^{14}\text{C}$  of  $67 \pm 9\text{‰}$  ( $n=68$ ). These  $\delta^{13}\text{C}$



values are similar to others reported in literature for marine phytoplankton (Peterson and Howarth 1987), however, a number of environmental factors (such as temperature, CO<sub>2</sub> concentration and  $\delta^{13}\text{C}$ -DIC signature) have been shown to affect isotopic fractionation by primary producers, resulting in a larger range of  $\delta^{13}\text{C}$  values for microalgae (Fogel et al. 1992; Currin et al. 1995; Laws et al. 1995).

While some DOC end members to the SAB had very distinct isotopic signatures, such as riverine and deep Gulf Stream waters (>~400 m) (Figure 32B), overlap between the salt marsh creek DOC and the phytoplankton-derived DOC end-member isotopic compositions must be reconciled before the contributions of these can be unequivocally delineated. The salt marsh creek samples most likely represent a composite of multiple primary producers, including emergent C<sub>3</sub> and C<sub>4</sub> plants, phytoplankton, and benthic micro- and macroalgae sources. Similar ambiguities were also encountered in previous studies, where overlap between the isotopic signatures of benthic micro- and macroalgae and salt marsh plants resulted in ambiguity in the contributions from these end-members to POM exported from salt marshes (Haines 1976; Peterson and Howarth 1987).

Based on the earlier consideration of salinity-isotope relationships (Figures 29A-C) and DOM property-property plots (Figures 30A-B and 31A-B), the data suggest that inner shelf stations were influenced by both riverine and salt marsh end members. These inner shelf samples had higher DOC:DON ratios, depleted  $\delta^{13}\text{C}$ -DOC values and enriched  $\Delta^{14}\text{C}$ -DOC signatures (Figures 29A-C, 30A-B, 31A-B, and 32A) – attributes suggesting greater relative contributions from river and marsh material than from phytoplankton. In contrast, mid- and outer shelf stations were characterized as having relatively lower DOC:DON ratios and enriched  $\delta^{13}\text{C}$ -DOC signatures (Figures 29A-B, 30A-B, 31A-B, and 32A) that are more reflective of planktonic contributions. Therefore, when calculating the dual isotope mass balance, which can only solve for contributions from the three most likely sources at a time, SAB shelf surface samples were separated into inner shelf stations, and mid- plus outer shelf stations. The inner shelf solution was

calculated using salt marsh, river, and Gulf Stream sources of DOC, while the mid- and outer shelf stations were assumed to derive their DOC primarily from rivers, Gulf Stream waters and shelf phytoplankton sources. However, this represents a potential source of uncertainty to the model solutions, in that it allows for the presence of riverine DOC at mid- and outer shelf stations, but not salt marsh DOC. Nonetheless, on the basis of the existing information, the three end-member chosen for each region (inner and mid plus outer shelf) appear to be the best fits.

Results of the DOC dual isotope mass balance calculations are summarized in Table 7. At inner shelf stations in March and July, the DOC was estimated to be composed of ~26 to 51% riverine, ~25 to 44% salt marsh, and ~11 to 39% offshore Gulf Stream sources, while mid- and outer shelf samples during these two periods were estimated to consist of ~53 to 78% Gulf Stream, ~11 to 33% phytoplankton, and ~7 to 26% riverine DOC sources (Table 7). In October 2005, when it is hypothesized that OM exports from salt marshes were highest (Wang and Cai 2004), estimates of sources contributing to inner shelf DOC were ~50 to 80% salt marsh and ~20 to 50% riverine DOC materials at stations C01 and B01. At station D02, DOC was comprised of ~45% salt marsh, ~25% riverine, and ~30% Gulf Stream DOC, indicating this station was more similar to outer shelf stations during this particular time of year. These findings for D02 are also consistent with the reversal of water flow in the during fall in the SAB (Lee et al. 1991). Finally, outer shelf stations in October were estimated to be comprised of up to ~35 to 71% Gulf Stream, ~19 to 49% phytoplankton and ~9 to 26% riverine DOC sources. While a similar dual isotopic mass balance approach has been used previously for the MAB (Bauer et al., 2000; 2002), the notable absence of a significant marsh source to the MAB resulted in the dominance of the DOC pool by river, offshore and shelf phytoplankton sources only. Thus, the presence and persistence of a marsh component to the DOM pool and other pools (see below) in the SAB may be a significant defining feature of this ocean margin system.

## ***POC Sources and Behavior in the SAB***

### POC-Salinity Mixing Relationships

The physical and chemical factors affecting the distributions and C isotopic characteristics of DOC and POC are likely unique for each of these two pools of OM. Previous observations of  $\delta^{13}\text{C}$ - and  $\Delta^{14}\text{C}$ - DOC and POC indicate that they have highly disparate sources and residence times as a result of their physical and chemical properties and biogeochemical processing (Hedges et al. 1997; Bauer et al. 2002). POC concentrations followed a similar across-shelf decreases as DOC concentrations, with the highest values (up to 698  $\mu\text{g/L}$ ) on the inner shelf, and decreasing at mid- and outer shelf stations (to lows of  $\sim 20$   $\mu\text{g/L}$ ) (Figures 8A-C). This inner shelf maximum is likely due to riverine inputs of terrestrial and marsh-derived materials (Wang et al. 2004) as well as resuspension of bottom sediment in shallow shelf waters (Nittrouer and Wright 1994). Farther out on the shelf, as estuarine and oceanic waters mix in the frontal zone, POC concentrations decreased (Yoder 1985).

Similar to DOC concentrations, highly elevated POC concentrations were present in both river (mean =  $1232 \pm 778$   $\mu\text{g/L}$ ,  $n=4$ ) and salt marsh creeks (mean =  $1720 \pm 322$   $\mu\text{g/L}$ ,  $n=3$ ) waters. Again, for consistency, riverine and marine sources were chosen as the end members for POC-salinity mixing relationships. POC concentrations were not strongly correlated with salinity (Figure 33A), but instead suggested a number of different sources of POC throughout the SAB as seen in the deviation between the linear regression line for all surface samples (red dotted line) and the conservative mixing line (black solid line). Samples above the conservative mixing line indicate a source of POC to the SAB, most likely originating from salt marsh creeks, and which also lay above the conservative mixing line (Figure 33A).

$\delta^{13}\text{C}$ -POC vs. salinity relationship also exhibited deviations from the conservative mixing curve (black solid line), as evidenced by the position of the linear regression line

for all surface samples (red dotted line; Figure 33B). Stations with  $S < \sim 35$  were enriched with  $^{13}\text{C}$  relative to the predicted conservative riverine end member mixing curve (Figure 33B), again most likely due to salt marsh POC sources. Samples from higher salinity stations ( $S > \sim 35$ ) generally followed the conservative mixing curve (Figure 33B) suggesting that mid- and outer shelf stations were influenced to a greater extent by marine POC sources rather than salt marsh POC sources.

For  $\Delta^{14}\text{C}$ -POC vs. salinity, the linear regression line for all surface samples (red dotted line) closely follows the conservative mixing curve between riverine and marine end members (black solid line; Figure 33C) suggesting conservative mixing processes. Lower salinity stations ( $S < \sim 35$ ) generally followed the conservative mixing line, as did the salt marsh creek end member with the exception of one unique salt marsh sample, which was highly  $^{14}\text{C}$ -depleted ( $-321\text{‰}$ ). It is suspected this sample may have been influenced by aged peat that may have eroded from the surrounding marsh (Raymond and Hopkinson 2003). In contrast, higher salinity ( $S > \sim 35$ ) outer shelf samples tended to be depleted in  $^{14}\text{C}$ , indicating a potential Gulf Stream influence on POC isotopic composition at these stations (Figure 33C), or resuspension of aged sediment particles as has been observed in the MAB (Bauer et al. 2002). The influence of these aged sources of POC was most pronounced at high salinity stations in October 2005 (Figure 33C).

#### Relationships Between POC Properties

In contrast to the  $\Delta^{14}\text{C}$  vs.  $\delta^{13}\text{C}$  relationship for DOC (Figure 32A),  $\Delta^{14}\text{C}$ -POC vs.  $\delta^{13}\text{C}$ -POC for all SAB surface samples were positively correlated (Figure 34A). These findings suggest that terrestrial and riverine sources of DOC and POC, while both relatively enriched in  $^{13}\text{C}$ , show the opposite pattern in  $^{14}\text{C}$  distributions. That is, terrestrial/riverine DOC is modern and  $^{14}\text{C}$  enriched, while terrestrial/riverine POC is slightly depleted in  $^{14}\text{C}$ . Conversely, enriched  $\delta^{13}\text{C}$ -POC also tended to correspond to enriched  $\Delta^{14}\text{C}$ -POC (Figure 34A) implying that POC of marine origin tends to be more

modern. While POC isotopic signatures did not show any consistent spatial changes, there were significant temporal variations previously discussed in specific shelf regions for specific C isotopes. Generally, in the POC component, March and July surface samples had “younger”  $\Delta^{14}\text{C}$  signature (mean of all March and July  $15 \pm 35\text{‰}$ ,  $n=17$ ) and a larger range of  $\delta^{13}\text{C}$  values ( $-18.5\text{‰}$  to  $-22.6\text{‰}$ ; Figure 34A) suggesting that a variety of modern sources were contributing to POC at that time. In contrast, October samples were generally more depleted of  $^{14}\text{C}$  ( $\Delta^{14}\text{C}$  mean of all October  $-36 \pm 33\text{‰}$ ,  $n=11$ ) and had more similar  $\delta^{13}\text{C}$  values ( $-20.5\text{‰}$  to  $-22.1\text{‰}$ ; Figure 34A) suggesting that POC sources were “older” and less variable during this period possibly indicating greater terrestrial exports. In a manner analogous to the similarity in  $\Delta^{14}\text{C}$ -DOC vs.  $\delta^{13}\text{C}$ -DOC in both the SAB and MAB (see above), the  $\Delta^{14}\text{C}$ -POC vs.  $\delta^{13}\text{C}$ -POC in the MAB (Bauer et al. 2002) showed a similar positive relationship to that for the SAB, further suggesting that the source and age distributions of this pool of organic matter may be a common feature across temperate shelves having significant terrestrial/riverine inputs.

#### POC Isotopic Mass Balance

Further evaluation of the relationship between  $\Delta^{14}\text{C}$ -POC vs.  $\delta^{13}\text{C}$ -POC requires inclusion of potential end member sources to the POC pool (Figure 34B). Phytoplankton values were estimated from DIC  $\Delta^{14}\text{C}$  and  $\delta^{13}\text{C}$  values, as described above for the DOC isotopic mass balance. Also similar to the DOC isotopic mass balances, there was overlap between two of the POC end members, where salt marsh and riverine POC sources had similar  $^{14}\text{C}$  isotopic signatures (Figure 34B). Instead of attempting to differentiate between these sources, a river/marsh mean was used to describe the terrestrial component in the isotopic mass balance calculations (where mean  $\delta^{13}\text{C} = -27.8 \pm 3.9\text{‰}$ ,  $n=7$ ; and mean  $\Delta^{14}\text{C} = -18 \pm 22\text{‰}$ ,  $n=6$ ). The salt marsh POC sample from Hudson Creek ( $\Delta^{14}\text{C}=-321\text{‰}$ ) was excluded from the  $\Delta^{14}\text{C}$  mean due to its highly anomalous nature relative to the other marsh samples, and because this sample also

overlaps with the Gulf Stream end member, further complicating the mass balance analysis. The mean terrestrial  $\delta^{13}\text{C}$ -POC signature was similar to  $\delta^{13}\text{C}$ -POC signatures of  $\sim -28\text{‰}$  reported by Otero et al. (2000) for fresh water portions of the Altamaha and Satilla Rivers (Georgia, USA).

Results of the POC dual isotope mass balance calculations are summarized in Table 7. Phytoplankton sources dominated the POC isotopic composition throughout the year, and especially at outer shelf stations (Table 7, Figure 34B). At inner shelf stations, POC was estimated to be composed of  $\sim 2$  to 29% terrestrial,  $\sim 0$  to 37% Gulf Stream and  $\sim 58$  to 77% phytoplankton POC sources. At mid- and outer shelf regions, POC composition was calculated as  $\sim 0$  to 51% terrestrial,  $\sim 0$  to 40% Gulf Stream and  $\sim 49$  to 100% phytoplankton POC sources. The somewhat elevated levels of terrestrial materials in certain POC samples at mid- and outer shelf stations may be a result of periodic sediment particle resuspension that has been found to be a common feature of such shelf environments (Nittrouer and Wright 1994).

### ***DIC Sources and Behavior in the SAB***

#### **DIC-Salinity Mixing Relationships**

DIC concentrations vs. salinity (Figure 35A) showed significant deviations from conservative mixing between freshwater and marine end members throughout the SAB, as evidenced by the linear regression line (dotted red line) for all upper water column samples ( $< \sim 50$  m) which lies above the conservative mixing line (solid black line) indicating that there was excess DIC on the SAB shelf in 2005. Deeper shelf/slope waters ( $> \sim 50$  m) were also distributed above the conservative mixing line further indicating excess DIC (Figure 35A) to these waters. In addition, both salt marsh and estuarine sources were above the conservative mixing line suggesting that these systems may be sources of DIC to the SAB shelf (Figure 35A). An alternative analysis using one of these sources as the end member instead of the freshwater rivers would yield different

results, such as more conservative mixing if the estuarine end member was used or possibly a sink for DIC if the salt marsh end member was used. For simplicity and consistency, the freshwater riverine end member was again chosen for all mixing relationships.

DIC isotopic mixing curves can be used as an indicator of net-heterotrophic or net-autotrophic processes in a system, since deviations from the mixing line may reflect biological activity and/or atmospheric exchange (Spiker 1980; Coffin et al. 1994). In the  $\delta^{13}\text{C}$ -DIC vs. salinity relationship (Figure 35B), SAB shelf samples consistently fell below the conservative mixing curve (solid black line) and as shown by the linear regression line (dotted red line) for all upper water column samples ( $<\sim 50$  m). This suggests a possible significant addition of biogenic  $\text{CO}_2$  (i.e., from heterotrophic processes; Spiker 1980; Coffin et al. 1994). Estuarine samples plotted both above and below the conservative mixing curve with one higher salinity ( $\sim 25$ ) sample consistent with inner shelf  $\delta^{13}\text{C}$ -DIC values (Figure 35B). Salt marsh sources were  $\sim 2\text{‰}$  depleted in  $\delta^{13}\text{C}$ -DIC relative to inner shelf samples (Figure 35B), suggesting that marsh DIC influences the  $\delta^{13}\text{C}$ -DIC signature on the inner shelf.

In the  $\Delta^{14}\text{C}$ -DIC vs. salinity relationship, deviations from conservative mixing will vary as a function of equilibrium with atmospheric  $\text{CO}_2$ , and carbonate mineral dissolution (Spiker 1980). Similar to the  $\delta^{13}\text{C}$ -DIC vs. salinity relationship, the vast majority of SAB shelf samples were  $\Delta^{14}\text{C}$  depleted relative to the conservative mixing curve (solid black line) and as shown by the linear regression for all surface samples ( $<\sim 50$  m; red dotted line; Figure 35C). Deep waters ( $>\sim 50$  m depth) of slope stations had a large range of  $\Delta^{14}\text{C}$  values, some more enriched than surface waters ( $\sim 87\text{‰}$ ) and others which were depleted ( $\sim 75\text{‰}$ ) and had  $\Delta^{14}\text{C}$ -DIC values lower than the Gulf Stream end member ( $\sim 30\text{‰}$ ; Figure 35C); these deep water samples could not be adequately assessed by the isotopic mass balance approach used here due to uncertainties in the most appropriate end members for these waters. Salt marsh creek samples were depleted in

$\Delta^{14}\text{C}$  relative to the conservative mixing line (Figure 35C), suggesting that these may have been contributing to shelf DIC. Estuarine end members were more highly depleted in  $^{14}\text{C}$  relative to the conservative mixing line (Figure 35C), suggesting that other processes, possibly carbonate mineral dissolution, was contributing to the  $\Delta^{14}\text{C}$  signatures in this region (Spiker 1980).

#### Relationships Between DIC Properties

The  $\Delta^{14}\text{C}$ -DIC vs.  $\delta^{13}\text{C}$ -DIC relationship for all SAB samples shows additional differences between upper ( $<\sim 50$  m) and deep ( $>\sim 50$  m) water masses (Figure 36A). The correlation for all surface samples yields a positive relationship (Figure 36A). Upper water column samples ( $<\sim 50$  m) with depleted  $\delta^{13}\text{C}$ -DIC were also relatively depleted in  $\Delta^{14}\text{C}$ -DIC, suggesting possible contributions from respiration of slightly older  $^{14}\text{C}$ -depleted materials (Spiker 1980). Upper water column samples ( $<\sim 50$  m) with enriched  $\delta^{13}\text{C}$ -DIC signatures were also relatively more enriched with  $\Delta^{14}\text{C}$ -DIC (Figure 36A). Deep water samples ( $>\sim 50$  m) had similar  $\delta^{13}\text{C}$ -DIC signatures (mean =  $0.9 \pm 0.2\text{‰}$ ,  $n=43$ ) and a large range of  $\Delta^{14}\text{C}$ -DIC signatures, from  $-74$  to  $87\text{‰}$  (Figure 36A) with the more depleted  $\Delta^{14}\text{C}$ -DIC signatures indicating the presence of “older” Gulf Stream waters (Severinghaus et al. 1996).

#### DIC Isotopic Mass Balance

The relevant isotopic end-members for carbon sources potentially contributing to the DIC in the SAB (Figure 36B) suggest that SAB surface waters are relatively well-constrained by air-sea exchange of  $\text{CO}_2$ , river, estuarine and salt marsh sources and deeper offshore waters that mix with slope and shelf waters. The air-sea exchange term was bounded for  $\Delta^{14}\text{C}$  by using the known  $\Delta^{14}\text{C}$  of 2005 atmospheric  $\text{CO}_2$  for the eastern U.S. ( $55$  to  $66\text{‰}$ ; Hsueh et al. 2007) corrected for equilibrium isotopic fractionation (Stuiver and Polach 1977). The  $\delta^{13}\text{C}$  for atmospheric  $\text{CO}_2$  in 2005 was estimated to have



a signature of  $\sim -8.5\text{‰}$ . Estimating the  $\delta^{13}\text{C}$  of seawater DIC resulting from atmospheric exchange has a range of uncertainty due to equilibrium fractionation, which varies primarily as a function of water temperature; for the temperature range of SAB waters, a fractionation factor of  $-8$  to  $-10\text{‰}$  (mean of  $\sim -9\text{‰}$ ) is appropriate (Broecker and Peng 1982). All other isotopic signatures of potential DIC sources were measured directly as part of this study (Table 5; Figure 36B).

Based on the known or identified end members and DIC-salinity relationships (Figures 35A-C), relative contributions to the DIC pool were estimated using salt marsh creeks, surface ocean  $\text{CO}_2$  exchange and deep Gulf Stream ( $>900$  m) waters as end members. For purposes of simplification, it was assumed that marsh creek waters would also contain river and estuarine components, and thus serve as a better integrated end-member of all three of these potential sources. While this may not adequately reflect all processes occurring in the DIC pool on the SAB shelf in 2005, it was felt to be the best estimate based on the constrained parameters. It is also important to note that a number of the samples have  $\Delta^{14}\text{C}$ -DIC values that exceed the atmospherically equilibrated DIC source (Figure 36B). One possibility for these elevated values is the preferential respiration of  $^{14}\text{C}$  enriched riverine or marsh DOC in SAB shelf waters. However, these DOC components are not included due to the complexity of the seawater DIC system and limitations of the three-end member approach.

Isotopic mass balance results for SAB DIC surface samples are summarized in Table 7. On the inner shelf, especially at station C01, there was an increase in the relative contribution of salt marsh sources as the year progressed. In March and July 2005, inner shelf waters were calculated to be comprised of  $\sim 50$  to  $66\%$  modern DIC in equilibrium with atmospheric  $\text{CO}_2$ ,  $\sim 23$  to  $49\%$  salt marsh DIC and up to  $\sim 16\%$  offshore Gulf Stream DIC. At mid- and outer shelf stations during this same time, there was a calculated decrease in the relative contribution of salt marsh DIC (up to  $\sim 20\%$ ) as the

relative Gulf Stream and atmospheric source strengths increased (up to ~30% and 66 to 100%, respectively).

The “marsh CO<sub>2</sub> pump hypothesis” states that in the fall, there is a large efflux of CO<sub>2</sub> and DIC and possibly organic matter from the coastal salt marshes into the SAB shelf (Wang and Cai 2004). Evidence for this was found from the dual isotope mass balance estimates for the inner shelf during October 2005, where salt marsh DIC sources contributed up to ~52% of the total DIC pool, while atmospherically equilibrated seawater DIC contributed ~53 to 87%, and the Gulf Stream influence was up to ~18% (Table 7). However, the impact of salt marsh inputs on the isotopic composition of DIC did not persist into the mid- and outer shelf surface waters. At these locations, DIC was instead estimated to be comprised predominantly of atmospherically equilibrated seawater DIC (~77 to 87%, Table 7), with smaller contributions from deep Gulf Stream waters (~10-20%) and no more than ~13% salt marsh DIC.

### ***Shelf DOM Dark Decomposition Experiments***

#### **DOC Decay Rates and Stoichiometry**

While not all of the dark incubation experiments were successful due to contamination of some of the nearly year-long time series (data not shown), the majority of the incubations (Figures 23A-C) showed consistent time-dependent decreases in DOC concentrations. Results from the March 2005 decomposition time series (Figure 23A) displayed the highest DOC decay rate coefficients (mean  $k=0.00118 \pm 0.00011 \text{ day}^{-1}$   $n=2$ ; Table 6) at the outer shelf station. Inner shelf stations during this time showed essentially no change, which suggests that the DOC originating from river or marsh sources during this period of high discharge may have been largely unreactive.

In July and October 2005, however, larger decreases in DOC concentrations occurred at the inner compared to mid shelf stations (Figures 23B and C, respectively), yielding higher decay rate coefficients (inner shelf means for July and October,

$k=0.00032 \pm 0.00001 \text{ day}^{-1}$  and  $k=0.00085 \pm 0 \text{ day}^{-1}$  respectively,  $n=2$ ; Table 6), and indicating that terrestrial sources of DOC may have been a source of relatively reactive material during the summer and fall. Mid- and outer shelf stations in the summer were deduced to be comprised primarily of a background, and presumably refractory, DOC pool, since there were no net changes in DOC concentration in these containers (Figures 23B and 24A). The October outer shelf time series, where large and consistent increases in DOC concentration occurred (Figures 23C and 24C), suggest that there may have been micro-organisms present in these waters with the ability to fix  $\text{CO}_2$  in the absence of light and produce DOC. In all July and October 2005 experiments, concentrations of DON decreased (Figures 24B and D), indicating the preferential remineralization of this component.

DOC:DON ratios of the initial and final samples for July and October (Figures 37A-B) offer further evidence of preferential DON utilization during DOM decomposition in the SAB. All incubations exhibited an increase in DOC:DON, albeit to different extents. At inner shelf stations where there were the largest decreases in DOC concentration and moderate decreases in DON concentration, the DOC:DON showed the smallest change (Figures 37A-B), although it was still significantly different from initial DOC:DON (one-way ANOVA,  $P<0.01$ ,  $n=4$ , for both July and October series). At mid-shelf stations during both experiments, there was little change in DOC concentration and the largest decrease in DON concentration (Figures 24A-D), resulting in a larger increase in DOC:DON ratio (Figures 37A-B; one-way ANOVA,  $P<0.01$ ,  $n=4$ , for both July and October series).

The outer shelf station in October showed a dramatic increase in DOC:DON (one-way ANOVA,  $P<0.01$ ,  $n=4$ ,) due to the simultaneous decreases in DON concentration and increases in DOC concentration (Figures 24C-D). While it is difficult to envision the mechanisms responsible for preferential production of DOC and loss of DON, they would presumably need to rely on the utilization of substrates in which C and N are

uncoupled from one another. Finally, these results suggest that in July and October, reactive DOC was recycled on the inner shelf, while on the mid- and outer shelf regions DOC was relatively refractory and DON was the preferred component utilized by heterotrophic bacteria in the SAB (Table 6; Figures 37A-B).

Similar dark decomposition experiments have been conducted previously in the MAB where the spatial and stoichiometric patterns of DOC, DON, and DOP reactivity were examined (Hopkinson et al. 1997; Hopkinson et al. 2002). Time series plots of DOC utilization in the MAB showed similar logarithmic decreases (Hopkinson et al. 1997; Hopkinson et al. 2002) to the SAB decomposition experiments (Figures 23A-C). However, DOC decay rate coefficients in surface waters of the MAB were about two-fold higher than in the SAB (up to  $0.0025 \text{ day}^{-1}$  for MAB vs.  $0.00118 \text{ day}^{-1}$  in the SAB), with the highest rates occurring at inner shelf stations and the lowest rates at outer shelf and deep water stations in both regions (Hopkinson et al. 1997). All MAB incubations resulted in increases in DOC:DON ratios, similarly indicating preferential remineralization of DON to DOC (Hopkinson et al. 1997; Hopkinson and Vallino 2005).

Several studies in the SAB have shown that photodegradation may be a significant sink for DOM and may increase both the rate and extent of bacterial decomposition (Miller and Zepp 1995; Miller and Moran 1997; Obernosterer and Benner 2004). For example, Miller and Moran (1997) found that photochemical reactions may “condition” DOM in SAB surface waters and stimulate bacterial decomposition, ultimately controlling the rate of biological consumption of the more refractory components of the DOM pool. Using the decay rate coefficients calculated from the DOM decomposition experiments in this study as an indicator of reactivity of DOM in the absence of photodegradation processes (Table 6), it appears that during the summer and fall months DOC was relatively reactive at inner shelf stations and relatively refractory at mid shelf stations. In the winter, and possibly spring, months, the calculated decay rate coefficients (Table 6, Figure 23A) suggest that DOC may be more refractory

along the inner shelf during periods when greater amounts of riverine materials were exported onto the shelf and more reactive at mid- and outer shelf regions where phytoplankton sources were more dominant.

Those samples that exhibited decreases in DOC from heterotrophic bacterial activity may have been further limited by low inorganic nutrient concentrations or a lack of bioavailable DOC substrates. Results from short term incubations of Altamaha and Savannah River water, for example, suggest that the biochemical composition of riverine DOM may affect its utilization by bacteria, rather than inorganic nutrient availability (Sun et al. 1997; Moran et al. 1999; Wiegner et al. 2006). It has also been suggested that in rivers DON degrades relatively more rapidly and supports more bacterial production than DOC (Wiegner et al. 2006). Results from these SAB shelf experiments are therefore consistent with findings in other coastal and river systems that the relative amount of DON utilized tends to be greater than that for DOC, leading to significant increases in the DOC:DOC of the remaining, more refractory material (Table 6; Figures 24A-D and 37A-B).

#### $\Delta^{14}\text{C}$ -DOC Changes and Mass Balances During DOM Dark Decomposition

In order to isotopically characterize the component of DOC utilized by heterotrophic bacteria and help establish its source, simple isotopic mass balance calculations were conducted using the initial and final DOC concentrations and  $\Delta^{14}\text{C}$  isotopic signatures. This exercise was not attempted on the  $\delta^{13}\text{C}$  results as these showed nominal changes during the course of DOC decomposition (Figure 25A). However, calculated  $\Delta^{14}\text{C}$  values of the utilized fractions (Table 8) were significantly enriched over either the starting or ending DOC, with a mean of  $405 \pm 100\text{‰}$  ( $n=2$ ) at the inner shelf site and  $1029 \pm 411\text{‰}$  ( $n=2$ ) at the mid shelf site. These highly enriched values indicate that heterotrophic bacteria preferentially utilized components of the bulk DOC with  $\Delta^{14}\text{C}$  values indicative of significant bomb  $^{14}\text{C}$ , and, in the most enriched case, these values

were similar to the maximum atmospheric bomb  $\Delta^{14}\text{C}$  signal attained in the period immediate following nuclear weapons testing (Keeling et al. 1995; Krakauer et al. 2006), and which would have imparted these same elevated signatures to terrestrial plant materials. These highly enriched  $\Delta^{14}\text{C}$  signatures for the utilized DOC components may also be in part a result of limitations of the simple 2-end member isotopic mass balance model that is traditionally used in these types of calculations.

Few similar DOC utilization experiments exist with which to compare these SAB findings. However, in the upper, low salinity ( $S < 4$ ) portion of the York River estuary, VA, Raymond and Bauer (2001a) calculated similarly  $\Delta^{14}\text{C}$ -enriched values of utilized DOC fractions (385‰ to 698‰). These workers were also unable offer a specific process or mechanism that would result in calculated utilized DOC components having  $\Delta^{14}\text{C}$  signatures greater than  $\sim 450$ ‰. However, the occurrence of this phenomenon in several systems would appear to warrant a closer examination of both the microbial processes and sources of DOC that could lead to such a highly  $\Delta^{14}\text{C}$ -enriched utilized fraction.

### ***Sources and Cycling of Carbon and Organic Matter in the SAB***

The SAB ocean margin has been previously characterized as being a net heterotrophic system (Hopkinson 1985; Cai et al. 2003; Wang et al. 2005). The “marsh  $\text{CO}_2$  pump” hypothesizes that in the spring and early summer, coastal salt marshes of Georgia accumulate  $\text{CO}_2$  from the atmosphere by assimilating it into organic matter via photosynthesis (Wang and Cai 2004). It further hypothesizes that as summer progresses, marsh primary production decreases and respiration increases, resulting in marsh export of inorganic and organic carbon to adjacent estuaries and coastal waters (Wang and Cai 2004), potentially fueling heterotrophic conditions in the SAB (Wang et al. 2005). Similarly, Hopkinson (1985) noted a seasonal relationship between respiration and

temperature, but not respiration and photosynthesis, suggesting the importance of allochthonous materials in the nearshore region.

Several lines of evidence presented in the current study are consistent with the classification of the SAB as a heterotrophic margin (Hopkinson 1985; Cai et al. 2003) as well as the “marsh CO<sub>2</sub> pump” hypothesis (Wang and Cai 2004). Results from this study illustrate year-round across-shelf gradients in carbon and organic matter distributions and associated parameters and OM recycling in surface waters. In addition, temporal changes in the magnitudes and sources of terrestrial inputs to surface waters of inner shelf sites from winter/spring (March) to summer/fall (July and October) may also affect C and OM processing differently on the mid- and outer shelf compared to the nearshore SAB.

#### Regional Differences in C Sources and Cycling in the SAB

Inner shelf stations received significant inputs of DOC and POC from terrestrial sources as seen in the across-shelf concentration gradients (Figures 6A-C and 8A-C) and isotopic signatures (Figures 9A-C, 10A-C, 11A-C, and 12A-C) of both of these bulk pools. While DOC concentration-salinity plots suggested quasi-conservative mixing between riverine and marine end members (Figure 29A), the distributions of DOC isotopes vs. salinity suggested that there were additional sources of isotopically enriched DOM (i.e., for both  $\delta^{13}\text{C-DOC}$  and  $\Delta^{14}\text{C-DOC}$ ) at lower salinity shelf stations ( $S < \sim 32$ ; Figures 29B-C), which isotopically most resembled salt marsh creek DOM.

Inner shelf stations were generally characterized by depleted  $\delta^{13}\text{C-DOC}$  and enriched  $\Delta^{14}\text{C-DOC}$  (Figures 9A-C, 10A-C, and 32A) suggesting the presence and persistence of modern terrestrial derived DOC there. In contrast, mid- and outer shelf stations were characterized by greater relative amounts of  $\delta^{13}\text{C}$ -enriched and  $\Delta^{14}\text{C}$ -depleted DOC (Figures 9A-C, 10A-C, and 32A) indicating the presence of greater relative amounts of aged, marine DOC. Dual isotope mass balance estimates for the

DOC component further suggested a prevalence of terrestrial materials, both riverine and salt marsh sources, at inner shelf stations (Table 7; Figure 32B). Outer shelf stations, in contrast, tended to be dominated by marine phytoplankton and Gulf Stream sources (Table 7; Figure 32B). However, these results are still somewhat inconclusive as a result of isotopic similarity of the salt marsh creek and phytoplankton end members.

POC did not appear to mix conservatively between riverine and marine end members across the SAB shelf (Figure 33A) and was likely influenced by organic matter sources that isotopically also resembled salt marsh materials. Further evidence for a salt marsh source of POC to shelf waters was found in the  $\delta^{13}\text{C}$ -POC vs. salinity mixing curve (Figure 33B) where both lower salinity ( $S < \sim 35$ ) shelf and salt marsh samples were depleted in  $\delta^{13}\text{C}$  relative to the conservative mixing line between riverine and marine end members. In part due to the relatively small range of  $\Delta^{14}\text{C}$ -POC values in surface waters (Table 4),  $\Delta^{14}\text{C}$ -POC vs. salinity appeared to mix quasi-conservatively across the SAB shelf (Figure 33C), except at a few high salinity stations ( $S > \sim 35$ ) where Gulf Stream influences were likely influencing the  $\Delta^{14}\text{C}$  signature.

The overall isotopic composition of POC on the SAB shelf was suggestive of a combination of “older” terrestrial sources and “younger” marine sources (Figures 11A-C, 12A-C, and 34A). This is essentially opposite to the age-source contributions to the DOC pool in SAB waters, which was comprised predominantly of young terrestrial and old marine sources (Figures 9A-C, 10A-C, and 32A). Results of dual isotope mass balance of the POC pool suggested the dominance of recently produced phytoplankton sources throughout surface waters of the SAB (Table 7; Figure 34B). Thus, the general sources and ages of DOC and POC isotopic signatures are opposing each other in the SAB illustrating the highly disparate sources and processes affecting the cycling of each of these pools.

To further consider across-shelf changes in the cycling of DOC and POC, DIC concentrations and isotopic signatures may be useful as indicators of biological activity



and atmospheric exchange (Spiker 1980; Coffin et al. 1994). DIC concentration gradients in the upper water column (<~50 m) from this study did not suggest a terrestrial source of DIC to the shelf region (Figures 17A-C and 18A-C). Instead, the DIC concentration vs. salinity mixing relationship indicated that excess DIC was present on the SAB shelf relative to the conservative mixing line between freshwater riverine and marine end members (Figure 35A).  $\delta^{13}\text{C}$ -DIC in surface waters (<~50 m) was depleted on the inner shelf and increased at mid- and outer shelf stations (Figures 19A-C and 20A-C), suggesting that heterotrophic processes on the inner shelf, possibly driving some of the DIC excess (e.g., respiration of exported river and marsh organic matter exported to the SAB), and equilibrium exchange with the atmosphere at outer shelf stations (Spiker 1980; Coffin et al. 1994) are the dominant processes there.

Additionally, DIC isotope-salinity mixing relationships for both  $\delta^{13}\text{C}$ -DIC and  $\Delta^{14}\text{C}$ -DIC were strongly depleted relative to the conservative mixing distributions between freshwater riverine and marine end members (Figures 35B-C). These findings further suggest either a) the influence of salt marsh sources which also were depleted in both isotopes relative to the conservative mixing curve, b) heterotrophic processes depleting the DIC isotopic signatures, or c) a combination of both. Generally, in surface waters (<~50 m) of the SAB, lighter  $\delta^{13}\text{C}$ -DIC signatures corresponded with depleted (but still modern)  $\Delta^{14}\text{C}$ -DIC signatures and conversely, heavier  $\delta^{13}\text{C}$ -DIC signatures corresponded with enriched  $\Delta^{14}\text{C}$ -DIC signatures (Figure 36A). Dual isotope mass balances for the DIC pool suggested that at inner shelf stations, the DIC pool was comprised of relatively similar portions of salt marsh creek and seawater  $\text{CO}_2$  sources (Table 7; Figure 36B). The DIC concentration gradient would, however, appear to argue against a significant export term of  $^{13}\text{C}$ - and  $^{14}\text{C}$ -depleted DIC from rivers, estuaries and marshes to the SAB. Thus, we speculate that respiration of some combination of river, estuarine and marsh-derived DOC and POC is the most likely mechanism for generating the observed DIC isotopic distributions in the SAB, especially the inner shelf.

In summary, the distributions of carbon and organic matter, their respective isotopic distributions and mass balances, used to calculate the relative contributions of carbon and organic matter sources, all suggest that terrestrial and salt marsh materials had a measurable influence on the composition of DOC, POC and DIC pools on the inner shelf of the SAB (Table 7).

#### Heterotrophy and Organic Matter Alterations in the SAB

To evaluate potential coupling between organic matter and DIC in the SAB via autotrophic and heterotrophic processes, DIC and DOC concentrations and  $\delta^{13}\text{C}$  isotopic signatures were plotted as a function of one another (Figures 38A and B; Raymond et al. 2004). DIC vs. DOC concentrations were negatively correlated for all sampling periods (Figure 38A), suggesting that, overall, the processes producing and consuming the two, such as photosynthesis and heterotrophic respiration were inversely related. In contrast to concentrations,  $\delta^{13}\text{C}$ -DIC vs.  $\delta^{13}\text{C}$ -DOC for surface samples were positively correlated (Figure 38B). Stations with depleted  $\delta^{13}\text{C}$ -DOC also were depleted in  $\delta^{13}\text{C}$ -DIC (Figure 38B) suggesting the respiration of terrestrial sourced DOC. Similarly, stations with enriched  $\delta^{13}\text{C}$ -DOC also tended to be enriched  $\delta^{13}\text{C}$ -DIC (Figure 38B) further suggesting a coupling between the DOC and DIC pools via autotrophic and heterotrophic processes. In the SAB ocean margin, this coupling may be further exemplified by the strong across-shelf gradients, where heterotrophic processes dominate water column processes and hence, carbon and organic matter distributions and characteristics at inner shelf stations (Hopkinson 1985; Wang and Cai 2004), while at mid- and outer shelf stations, the system is closer to being metabolically balanced (Cai et al. 2003).

Significant temporal changes in carbon and organic matter distributions and elemental and isotopic characteristics in the SAB further suggest that the above general features may reflect important seasonal and climatological forcings that drive not only the inputs and characteristics of these materials, but ultimately their role in helping establish

the metabolic status of the SAB. This will be controlled not only by the reactive forms of allochthonous organic matter exported from landward of the land-ocean interface, but by the export (or import) of inorganic carbon as well (Ducklow and McCallister 2004; Borges 2005; Cai et al. 2006). Some of the strongest anomalies in organic matter distributions and both isotopic and elemental characteristics were observed for March 2005 when compared to July and October 2005 (Figures 26A-C, 30A-B, 31A-B, 32A-B, and 34A-B). March was also the highest river discharge period of the three cruises (Figures 5A-D), resulting in a flux of terrestrial organic matter in inner shelf waters during this part of the year.

Interestingly, much of the river, estuarine and/or salt marsh material that was exported to the inner SAB in spring did not appear to be particularly reactive, at least to dark heterotrophic processing (Table 6; Figure 23A). Instead, perhaps due to warmer summer and fall temperatures (Hopkinson 1985; Pomeroy et al. 2000), or “conditioning” of DOM by exposure to photochemical or other processes (Miller and Zepp 1995; Miller and Moran 1997; Obernosterer and Benner 2004), DOM reactivity in inner shelf waters appeared to be greatest in fall (Table 6; Figures 23C and 24C-D). In addition, the sources and ages of DOM supporting heterotrophic respiration on the inner and mid-shelf, if the October incubations are representative of the system in general, suggest that: a) a modern, bomb-enriched component(s) of DOM (Table 8), most closely resembling the  $^{14}\text{C}$ -enriched river and marsh DOM (Table 4), is in part supporting the heterotrophy, and hence, production of excess  $\text{CO}_2$  and DIC in the SAB (Cai et al. 2003; Wang and Cai 2004; Wang et al. 2005); b) the remineralization of this bomb  $^{14}\text{C}$ -enriched DOM is uncoupled to a significant extent from DON remineralization (Figures 37A-B), allowing for a greater recycling of the river- and marsh-derived DON components in SAB waters, and presumably supplementing new shelf production of both phytoplankton and benthic microalgae (Yoder 1985; Jahnke et al. 2005); and c) the river and marsh-derived DOM is effectively stripped of both its younger C and more N-rich components in the SAB

(Figures 25B and 37A-B), leaving a highly aged and N-poor form of DOM for export to the greater North Atlantic.

A conceptual model of carbon cycling based on the findings of this study is depicted in Figure 39 to illustrate the basic inputs and transformations of OM on the SAB shelf. Terrestrial inputs of both organic and inorganic carbon to the inner shelf region are dominated by river and/or salt marsh-derived materials. Heterotrophic conditions may therefore dominate in the nearshore SAB due to inputs of this young, allochthonous OM which are rapidly remineralized, as shown by concentration gradients of DOC and POC as well as from findings from the dark DOM decomposition experiments. As a result of this and factors such as physical mixing of offshore materials, the terrestrial OM isotopic signal is not apparent at outer shelf stations, but rather reflects the presence of more typically marine OM on the basis of its concentrations,  $\delta^{13}\text{C}$  and  $\Delta^{14}\text{C}$  signatures. The  $^{14}\text{C}$ -enriched respired component of the DOM of river and marsh origin is therefore inferred to be the component that drives the net  $\text{CO}_2$  air-sea efflux from SAB waters on the inner and perhaps mid-SAB shelf. The more refractory  $^{14}\text{C}$ -depleted component remaining after DOM degradation is then available for export from the SAB shelf to the open ocean for long term storage, and contributing to the continental shelf pump. It is thus possible that preferential degradation of DOM in ocean margins is responsible for both molecularly transforming and “pre-aging” previously young terrestrial OM inputs such that they more closely resemble the aged and presumably refractory DOM of the deep open ocean, prior to its shelf export.

DOM (as DOC) fluxes from ocean margins have been speculated to be one of the most globally important sources of material supporting the steady-state inputs of the aged, N-poor DOM reservoir of the deep open ocean (Bauer and Druffel 1998; Duarte and Prairie 2005). Both the age and DOC:DON of the residual, non-metabolized DOM from the October mid-shelf incubations closely resemble the steady-state ages and DOC:DON ratios of mixed-layer and mesopelagic DOM from the contiguous Sargasso

Sea (Bauer and Druffel 1998; Bauer et al. 2001; Loh et al. 2004), suggesting that both terrestrial and shelf material in margins may be “pre-aged” during decomposition, and constitute a potentially important form of pre-aged refractory DOM to the open ocean. Indeed, ocean margins, if represented by the SAB in general, may primarily serve as “reaction zones”, not only converting land-derived organic materials to CO<sub>2</sub> and supporting a net heterotrophic metabolic balance there, but also simultaneously increasing the age, and reducing the N content and presumably the reactivity of DOM exported to the open ocean.

## CONCLUSIONS

The SAB ocean margin has previously been characterized as a net heterotrophic system potentially fueled by the adjacent coastal salt marshes of the southeastern USA. The findings from the present study are consistent with this classification, displaying year-round across-shelf gradients in carbon and OM distributions and associated parameters as well as OM recycling in surface waters. In addition, temporal changes in the magnitudes and sources of terrestrial inputs to surface waters of inner shelf sites from winter/spring (March) to summer/fall (July and October) may also affect C and OM processing differently on the mid- and outer shelf compared to the nearshore SAB. Respiration of some combination of river, estuarine and marsh-derived DOC and POC is speculated to be the most likely mechanism for generating the observed OM and DIC isotopic distributions in the SAB.

In the SAB ocean margin, strong across-shelf gradients as well as the relationships between various parameters suggest coupling between OM and DIC pools. At inner shelf stations, terrestrial inputs of OM and heterotrophic processes dominate the water column processes, and hence, carbon and OM distributions and characteristics. In contrast, at mid- and outer shelf stations, the system appears to be closer to being metabolically balanced, even though allochthonous terrestrial OM was often present. If the SAB is representative of ocean margins in general, these findings suggest that these dynamic, transitional environments may primarily serve as “reaction zones”, converting land-derived, allochthonous organic materials to inorganic components, while simultaneously increasing the age and reducing the N content, and presumably the reactivity, of DOM exported to the open ocean.

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**Table 1. Station locations, sampling dates and hydrographic data for 2005 cruises to the SAB.**

Station Number <sup>a</sup>	Date	GMT <sup>b</sup>	Latitude/Longitude	Depth (m)	Temperature (°C)	Salinity	Density (σ-t)	O <sub>2</sub> (mL/L)	Fluorometer (μg/L) <sup>c</sup>	PAR (μE/m <sup>2</sup> s) <sup>c</sup>
<i>March 2005 cruise</i>										
A01	3/27/2005	1:54	28°31.128'N/ 80°28.726'W	2	20.4	35.7	25.2	5.0	0.3	11.4
				14	20.1	35.9	25.4	4.6	0.3	0.0
A04	3/27/2005	4:24	28°33.224'N/ 80°15.145'W	2	22.0	36.3	25.2	5.0	0.1	32.0
				30	20.8	36.4	25.6	4.0	0.2	0.9
A08	3/27/2005	9:27	28°39.118'N/ 79°38.130'W	3	25.4	36.3	24.2	4.6	0.0	123.1
				51	24.2	36.3	24.6	4.6	0.0	7.3
				151	20.3	36.4	25.7	4.2	0.0	0.0
				601	8.0	35.0	27.3	2.8	0.0	0.0
<b>B01</b>	3/26/2005	2:15	30°00.005'N/ 81°15.034'W	2	15.8	34.2	25.2	5.5	0.5	5.7
				17	15.5	34.5	25.5	5.4	0.5	0.0
<b>B07</b>	3/26/2005	8:08	29°59.958'N/ 80°32.681'W	3	19.5	36.1	25.8	4.9	0.2	20.7
				15	19.6	36.3	25.8	4.5	0.2	2.7
				38	19.6	36.3	25.9	4.4	0.1	0.0
<b>B11</b>	3/26/2005	13:52	29°59.928'N/ 79°51.001'W	2	24.9	36.2	24.3	4.6	0.0	0.0
				51	23.7	36.4	24.8	4.4	0.1	0.0
				150	20.2	36.5	25.8	3.7	0.0	0.0
				301	14.4	35.9	26.8	3.0	0.0	0.0
				497	7.9	35.0	27.3	2.8	0.0	0.0
				630	7.3	34.9	27.3	2.9	0.0	0.0
<i>Altamaha R.</i>	3/22/2005	13:10	31°17.933'N/ 81°11.819'W	2	14.9	30.4	22.4	5.9	0.3	0.0
<b>Sapelo R.</b>	3/23/2005	2:44	31°32.719'N/ 81°12.204'W	2	14.6	29.9	22.1	5.7	0.7	8.1
<b>C01</b>	3/23/2005	1:49	31°32.457'N/ 81°06.071'W	2	13.8	30.4	22.6	5.8	0.3	3.2
<b>C03</b>	3/23/2005	4:03	31°30.208'N/ 81°00.556'W	2	13.5	31.9	23.9	5.9	0.2	27.5
<b>C04</b>	3/23/2005	4:44	31°28.104'N/ 80°55.203'W	2	13.9	33.6	25.1	5.8	0.1	59.9
<b>C05</b>	3/23/2005	5:26	31°25.899'N/ 80°49.910'W	2	13.9	34.5	25.8	5.7	0.1	104.4

<sup>a</sup> Stations in bold font were analyzed for DIC, DOC, and POC isotopes. Stations in italic font were sampled only for DIC isotopes and DOC concentrations.

Altamaha and Sapelo Rivers were sampled at the river mouth, on the inner shelf (depth <~5 m and S<~30).

<sup>b</sup> Time is reported as Greenwich Mean Time.

<sup>c</sup> Fluorometer and PAR sensors were not always functioning properly, resulting in false readings of zero.

**Table 1. (cont.)**

Station Number	Date	GMT	Latitude/Longitude	Depth (m)	Temperature (°C)	Salinity	Density (σ-t)	O <sub>2</sub> (ml/L)	Fluorometer (µg/L)	PAR (µE/m <sup>2</sup> s)
C05	3/23/2005	5:26	31°25.899'N/ 80°49.910'W	19	13.8	34.9	26.2	5.7	0.1	7.1
C07	3/23/2005	6:50	31°21.533'N/ 80°39.181'W	3	14.4	35.4	26.4	5.6	0.0	99.8
C09	3/23/2005	8:50	31°17.509'N/ 80°28.240'W	21	14.4	35.8	26.7	5.6	0.1	17.2
C11	3/23/2005	10:48	31°11.635'N/ 80°14.528'W	3	14.9	36.1	26.8	5.5	0.0	71.1
C12	3/23/2005	11:58	31°08.270'N/ 80°06.027'W	31	14.7	36.1	26.9	5.5	0.1	5.8
C13	3/23/2005	13:12	31°03.974'N/ 79°55.264'W	3	17.1	36.3	26.5	5.4	0.0	63.9
C14	3/23/2005	15:00	31°01.403'N/ 79°48.933'W	39	15.8	36.4	26.8	5.3	0.2	0.8
C15	3/23/2005	16:08	30°58.063'N/ 79°40.215'W	2	17.8	36.3	26.3	5.3	0.1	26.9
C16	3/23/2005	18:18	30°52.018'N/ 79°25.694'W	46	16.1	36.4	26.8	5.3	0.1	0.1
D02	3/21/2005	11:33	32°54.466'N/ 79°28.747'W	3	21.8	36.3	25.3	4.8	0.1	5.0
D07	3/21/2005	16:00	32°27.101'N/ 79°05.815'W	71	17.6	36.4	26.4	5.1	0.1	0.0
D11	3/22/2005	20:23	31°58.432'N/ 78°42.634'W	2	22.8	36.2	24.9	4.9	0.2	0.0
				50	21.6	36.3	25.3	4.5	0.1	0.0
				149	16.9	36.3	26.5	3.1	0.0	0.0
				249	15.3	36.2	26.9	4.6	0.1	0.0
				2	24.3	36.2	24.5	4.6	0.0	0.0
				51	24.0	36.4	24.7	4.5	0.1	0.0
				151	19.7	36.4	25.9	3.7	0.0	0.0
				460	8.0	35.0	27.3	2.9	0.0	0.0
				3	25.1	36.1	24.1	4.5	0.0	0.0
				50	25.2	36.1	24.1	4.5	0.0	0.0
				151	23.3	36.8	25.2	3.8	0.0	0.0
				501	12.3	35.5	26.9	2.5	0.0	0.0
				765	8.4	35.2	27.3	2.3	0.0	0.0
				1	12.4	31.9	24.1	6.3	0.4	22.4
				9	11.6	34.0	25.9	5.8	0.6	0.0
				2	18.9	36.5	26.1	5.2	0.3	0.4
				31	17.8	36.5	26.4	5.1	0.4	0.0
				2	21.0	36.3	25.5	5.1	0.2	0.0
				26	19.8	36.3	25.8	4.6	0.2	0.0

**Table 1. (cont.)**

Station Number	Date	GMT	Latitude/Longitude	Depth (m)	Temperature (°C)	Salinity	Density ( $\sigma-t$ )	O <sub>2</sub> (ml/L)	Fluorometer ( $\mu\text{g/L}$ )	PAR ( $\mu\text{E/m}^2\text{s}$ )
D11	3/22/2005	20:23	31°58.432'N/ 78°42.634'W	51	19.0	36.3	26.0	4.3	0.1	0.0
				150	13.5	35.8	26.9	3.2	0.0	0.0
				298	9.1	35.1	27.2	2.8	0.0	0.0
				381	8.6	35.1	27.2	2.9	0.0	0.0
E01	3/20/2005	1:10	33°49.694'N/ 78°11.894'W	3	10.2	33.0	25.4	6.2	0.4	0.2
				13	10.5	34.4	26.4	5.9	0.6	0.0
E07	3/20/2005	7:40	33°15.262'N/ 77°47.228'W	3	21.7	36.3	25.3	4.8	0.1	152.4
				12	21.7	36.3	25.3	4.8	0.1	54.0
E11	3/20/2005	13:18	32°42.952'N/ 77°24.285'W	30	19.6	36.5	26.0	5.0	0.2	12.7
				3	22.0	36.3	25.2	4.8	0.1	0.0
				50	20.3	36.3	25.7	4.2	0.1	0.0
				151	13.9	35.8	26.8	3.0	0.0	0.0
E12	3/21/2005	21:11	32°04.527'N/ 76°59.099'W	300	10.5	35.3	27.1	3.0	0.0	0.0
				2	23.8	36.4	24.7	4.6	0.0	0.0
				52	22.7	36.5	25.2	4.6	0.1	0.0
				101	21.5	36.7	25.6	4.7	0.0	0.0
A01	8/3/2005	2:26	28°31.106'N/ 80°28.796'W	150	21.1	36.8	25.8	4.7	0.0	0.0
				500	17.9	36.5	26.4	4.1	0.0	0.0
				899	4.7	35.0	27.7	5.5	0.0	0.0
				2	28.9	36.1	22.9	4.1	0.0	0.5
A04	8/3/2005	5:03	28°33.275'N/ 80°15.039'W	12	26.8	36.1	23.6	3.9	0.3	0.0
				2	28.3	36.1	23.1	4.2	0.0	19.0
A08	8/3/2005	10:18	28°39.184'N/ 79°38.132'W	31	20.5	36.1	25.5	5.4	0.6	1.5
				1	30.1	35.9	22.4	4.0	0.0	139.6
				49	27.7	36.2	23.4	4.3	0.0	13.4
A08	8/3/2005	10:18	28°39.184'N/ 79°38.132'W	151	23.9	36.9	25.1	3.4	0.0	0.0
				302	14.9	36.0	26.7	2.8	0.0	0.0
				500	10.3	35.2	27.1	2.6	0.0	0.0
				693	6.2	34.9	27.5	3.2	0.0	0.0



**Table 1. (cont.)**

Station Number	Date	GMT	Latitude/Longitude	Depth (m)	Temperature (°C)	Salinity	Density (σ-t)	O <sub>2</sub> (ml/L)	Fluorometer (µg/L)	PAR (µE/m <sup>2</sup> s)
B01	8/2/2005	1:57	29°59.977'N/ 81°14.978'W	2	28.6	36.1	23.0	4.3	0.1	0.5
				15	27.6	36.1	23.3	4.0	0.4	0.0
B07	8/2/2005	7:46	29°59.995'N/ 80°32.633'W	1	28.7	36.1	23.0	4.2	0.0	78.5
				37	19.7	36.1	25.7	5.0	0.4	3.1
B11	8/2/2005	14:05	30°00.385'N/ 79°50.915'W	1	30.0	36.0	22.4	4.1	0.0	62.0
				50	27.4	36.3	23.5	4.3	0.0	2.5
				150	19.9	36.7	26.1	3.1	0.0	0.0
				300	14.5	35.9	26.8	3.1	0.0	0.0
				501	9.1	35.1	27.2	2.7	0.0	0.0
				639	8.0	35.0	27.3	2.8	0.0	0.0
<i>Sapleo R. 1</i>	7/30/2005	5:41	31°32.736'N/ 81°12.193'W	1	31.1	26.5	14.9	3.2	1.3	20.7
<i>Sapelo R. 2</i>	7/30/2005	6:13	31°32.230'N/ 81°10.580'W	1	31.0	27.9	16.1	3.3	1.1	116.7
<b>C01</b>	7/30/2005	7:06	31°32.393'N/ 81°05.929'W	2	30.5	32.1	19.4	3.7	0.8	115.7
<b>C03</b>	7/30/2005	7:59	31°30.208'N/ 81°00.594'W	2	30.1	34.0	20.9	4.0	0.4	135.0
<b>C05</b>	7/30/2005	9:31	31°25.912'N/ 80°49.991'W	2	30.6	34.1	20.8	4.3	0.2	159.3
<b>C07</b>	7/30/2005	11:05	31°21.637'N/ 80°39.247'W	2	30.0	35.1	21.8	4.1	0.1	169.1
<b>C09</b>	7/30/2005	12:32	31°17.280'N/ 80°28.447'W	21	26.9	36.0	23.5	4.4	0.1	15.9
<b>C11</b>	7/30/2005	14:28	31°11.651'N/ 80°14.566'W	34	24.6	36.1	24.3	4.6	0.1	5.3
<b>C13</b>	7/30/2005	16:18	31°04.922'N/ 79°57.192'W	2	28.9	36.1	22.9	4.2	0.0	16.8
<b>C15</b>	7/30/2005	18:25	30°57.964'N/ 79°40.221'W	36	25.8	36.1	23.9	4.7	0.2	2.2
				2	29.0	36.0	22.9	4.3	0.0	0.6
				46	15.0	35.9	26.6	3.1	0.1	0.0
				1	30.3	36.1	22.4	4.0	0.0	0.9
				50	26.5	36.3	23.8	4.4	0.0	0.0
				152	14.4	35.7	26.7	3.1	0.1	0.0
				300	8.5	35.1	27.2	2.7	0.0	0.0
				454	7.3	35.0	27.3	2.9	0.0	0.0
<b>C16</b>	7/31/2005	20:58	30°51.924'N/ 79°25.866'W	1	30.1	35.9	22.4	4.0	0.0	0.5
				52	27.8	36.2	23.3	4.4	0.0	0.0

**Table 1. (cont.)**

Station Number	Date	GMT	Latitude/Longitude	Depth (m)	Temperature (°C)	Salinity	Density ( $\sigma-t$ )	O <sub>2</sub> (ml/L)	Fluorometer ( $\mu\text{g/L}$ )	PAR ( $\mu\text{E/m}^2\text{s}$ )
C16	7/31/2005	20:58	30°51.924'N/ 79°25.866'W	150	20.8	36.8	25.9	3.3	0.0	0.0
				302	16.9	36.3	26.6	3.7	0.0	0.0
				497	9.7	35.2	27.1	2.6	0.0	0.0
				761	7.5	35.0	27.3	2.9	0.0	0.0
				2	28.2	34.9	22.2	4.2	1.1	26.8
D02	7/29/2005	3:36	32°54.484'N/ 79°28.774'W	8	27.4	35.3	22.8	4.2	1.2	0.8
				1	30.3	33.9	20.8	4.1	0.0	133.7
D07	7/29/2005	8:14	32°27.156'N/ 79°05.850'W	37	22.9	36.5	25.1	4.0	0.1	1.3
				2	30.1	36.0	22.5	4.1	0.0	25.0
D11	7/29/2005	13:51	31°58.359'N/ 78°42.559'W	51	29.1	36.0	22.8	4.2	0.0	2.6
				151	21.6	36.8	25.7	3.2	0.0	0.0
E01	7/28/2005	2:07	33°49.313'N/ 78°11.917'W	298	10.6	35.3	27.1	2.7	0.0	0.0
				375	9.5	35.2	27.2	2.7	0.0	0.0
E07	7/28/2005	8:52	33°15.204'N/ 77°47.324'W	2	29.4	34.5	21.6	4.1	0.1	0.4
				10	27.3	35.3	22.8	4.6	0.2	0.0
E11	7/28/2005	15:04	32°42.876'N/ 77°24.183'W	2	29.0	35.9	22.7	4.2	0.0	126.3
				31	23.9	36.3	24.6	4.6	0.1	8.2
T07a	8/4/2005	8:40	31°26.171'N/ 77°21.494'W	1	29.9	35.2	22.0	4.1	0.0	12.1
				51	20.7	36.1	25.4	5.3	0.1	0.0
A01	10/15/2005	16:13	28°30.744'N/ 80°29.138'W	149	12.3	35.6	27.0	2.8	0.0	0.0
				300	9.2	35.1	27.2	2.7	0.0	0.0
October 2005 cruise				453	7.2	35.1	27.5	3.8	0.0	0.0
				2	29.6	36.1	22.7	4.0	0.0	138.3
A01	10/15/2005	16:13	28°30.744'N/ 80°29.138'W	51	27.6	36.3	23.5	4.3	0.0	15.3
				151	22.7	36.8	25.4	4.2	0.0	0.0
A01	10/15/2005	16:13	28°30.744'N/ 80°29.138'W	301	19.5	36.7	26.2	4.1	0.0	0.0
				498	16.0	36.2	26.6	3.5	0.0	0.0
A01	10/15/2005	16:13	28°30.744'N/ 80°29.138'W	989	4.2	35.0	27.8	5.6	0.0	0.0
				0	27.2	34.1	21.9	2.2	0.0	22.3

**Table 1. (cont.)**

Station Number	Date	GMT	Latitude/Longitude	Depth (m)	Temperature (°C)	Salinity	Density (σ-t)	O <sub>2</sub> (ml/L)	Fluorometer (µg/L)	PAR (µE/m <sup>2</sup> s)
A01	10/15/2005	16:13	28°30.744'N/ 80°29.138'W	12	27.2	34.1	22.0	2.6	0.0	0.0
A04	10/15/2005	18:59	28°32.859'N/ 80°15.286'W	0	27.5	34.9	22.5	3.2	1.5	31.3
A08	10/16/2005	0:48	28°39.886'N/ 79°38.465'W	29	27.5	35.0	22.5	3.2	1.5	0.2
				0	28.9	36.1	22.9	3.1	0.0	6.2
				50	28.2	36.2	23.2	3.2	0.0	3.7
				150	22.3	36.8	25.5	2.4	0.0	3.5
				302	15.8	36.1	26.7	2.1	0.0	3.4
				500	9.0	35.1	27.2	1.8	0.0	3.1
A08	10/16/2005	0:48	28°39.886'N/ 79°38.465'W	758	6.6	34.9	27.4	2.0	0.0	2.9
B01	10/14/2005	15:12	29°59.831'N/ 81°15.029'W	2	26.4	31.7	20.5	3.3	1.6	21.3
				14	26.6	32.4	20.9	3.2	1.8	0.1
B07	10/14/2005	22:45	29°59.559'N/ 80°32.945'W	1	27.5	35.7	23.0	3.2	0.0	10.1
				36	27.5	35.7	19.8	3.2	0.0	1.2
B11	10/15/2005	5:09	30°00.918'N/ 79°51.350'W	1	28.5	36.1	23.1	3.2	0.0	3.8
				51	27.7	36.3	23.4	3.2	0.0	2.9
				152	19.2	36.6	26.2	2.5	0.0	2.8
				300	16.1	36.2	26.6	2.4	0.0	2.7
				499	8.7	35.1	27.2	1.9	0.0	2.7
				625	7.4	35.0	27.3	2.0	0.0	2.5
<i>Sapelo R.</i>	10/12/2005	0:32	31°32.625'N/ 81°11.233'W	3	26.1	25.9	16.2	3.0	2.6	0.4
C01	10/12/2005	1:22	31°32.308'N/ 81°05.922'W	2	26.1	29.3	18.7	2.3	0.0	0.7
C03	10/12/2005	2:19	31°30.036'N/ 81°00.765'W	1	26.3	32.3	20.9	3.3	4.3	1.0
C05	10/12/2005	3:58	31°25.764'N/ 80°49.772'W	2	26.7	34.2	22.2	3.4	2.0	0.7
C07	10/12/2005	5:40	31°21.546'N/ 80°39.363'W	2	27.0	35.0	22.7	3.3	0.9	0.8
				19	27.0	35.0	22.7	3.3	1.0	0.3
C09	10/12/2005	21:42	31°16.340'N/ 80°28.907'W	1	26.9	35.3	23.0	2.6	0.0	25.9
C11	10/13/2005	14:22	31°11.099'N/ 80°14.629'W	27	26.9	35.3	23.0	2.7	0.0	1.1
				1	26.9	35.4	23.1	3.3	0.9	31.0
				35	26.9	35.5	23.1	3.3	1.0	0.7
C13	10/13/2005	17:55	31°04.707'N/ 79°57.601'W	6	27.4	35.6	23.0	3.3	0.7	14.7

**Table 1. (cont.)**

Station Number	Date	GMT	Latitude/Longitude	Depth (m)	Temperature (°C)	Salinity	Density (σ-t)	O <sub>2</sub> (ml/L)	Fluorometer (µg/L)	PAR (µE/m <sup>2</sup> s)
<i>C13</i>	10/13/2005	17:55	31°04.707'N/ 79°57.601'W	43	27.4	35.6	23.0	3.3	1.0	0.4
<i>C15</i>	10/14/2005	3:34	30°57.893'N/ 79°40.187'W	2	28.4	36.1	23.1	3.2	0.0	3.3
				51	28.1	36.5	23.5	3.2	0.0	2.6
				149	22.2	36.9	25.6	2.5	0.0	2.5
				298	15.0	36.0	26.7	2.1	0.0	2.5
				466	8.9	35.1	27.2	1.9	0.0	2.4
<i>C16</i>	10/14/2005	1:16	30°51.986'N/ 79°25.958'W	2	28.8	36.0	22.9	3.3	0.2	2.1
				51	26.9	36.4	23.8	3.2	0.5	1.1
				149	22.9	36.9	25.4	2.6	0.1	1.1
				300	18.4	36.6	26.4	3.2	0.1	1.0
<i>C16</i>	10/14/2005	1:16	30°51.986'N/ 79°25.958'W	502	13.3	35.7	26.9	2.4	0.1	1.0
<b>D02</b>	10/10/2005	11:46	32°54.370'N/ 79°28.857'W	781	8.4	35.1	27.3	2.1	0.1	0.9
<b>D07</b>	10/10/2005	17:37	32°26.588'N/ 79°06.121'W	6	25.7	33.5	22.0	2.3	0.0	0.4
				0	27.7	36.0	23.2	3.7	0.0	55.4
				37	27.6	36.1	23.3	2.6	0.0	1.8
<b>D11</b>	10/10/2005	23:54	31°58.269'N/ 78°41.747'W	0	28.2	36.1	23.2	3.2	0.0	2.0
				50	27.7	36.2	23.4	3.2	0.0	1.2
				151	14.5	35.9	26.8	2.2	0.0	1.1
				300	9.5	35.2	27.2	2.0	0.0	1.1
				392	9.2	35.2	27.2	2.0	0.0	1.0
<b>E01</b>	10/8/2005	8:42	33°49.912'N/ 78°11.826'W	0	25.2	33.5	22.1	2.7	0.0	1.6
<b>E07</b>	10/9/2005	15:15	33°15.562'N/ 77°47.299'W	8	25.2	33.5	22.2	2.6	0.0	0.9
<b>E11</b>	10/9/2005	21:49	32°43.165'N/ 77°24.477'W	1	28.0	36.0	22.2	3.3	0.0	57.1
				27	27.5	36.2	22.2	3.2	0.0	3.8
				0	27.8	36.2	23.3	3.3	0.0	11.9
				50	25.4	36.3	24.2	3.0	0.0	0.7
				150	13.2	35.7	26.9	2.1	0.0	0.3
				299	9.3	35.2	27.2	2.0	0.0	0.3
				438	8.4	35.1	27.3	2.4	0.0	0.3

**Table 1. (cont.)**

Station Number	Date	GMT	Latitude/Longitude	Depth (m)	Temperature (°C)	Salinity	Density (σ-t)	O <sub>2</sub> (ml/L)	Fluorometer (µg/L)	PAR (µE/m <sup>2</sup> s)
T07a	10/16/2005	19:09	30°59.348'N/ 77°55.007'W	2	27.5	36.2	23.5	3.2	0.0	7.8
				51	27.5	36.2	23.5	3.2	0.0	4.7
				151	21.6	36.9	25.8	3.1	0.0	0.1
				301	18.8	36.6	26.3	3.1	0.0	0.1
				501	16.9	36.3	26.6	2.8	0.0	0.1
				899	5.2	35.0	27.7	3.2	0.0	0.1

**Table 2. Locations, sampling dates and hydrographic data for SAB river and salt marsh end members collected in July 2006.**

Site	Latitude/ Longitude	Sample Date	GMT	Temperature (°C)	Salinity	pH	DO (mg/L)
<i>Rivers</i>							
St Johns River, FL	30°10.05'N/ 81°38.85'W	7/11/2006	13:00	29.1	8	7.62	4.0
Altamaha River, GA	31°21.47'N/ 81°26.58'W	7/11/2006	14:15	30.2	3	7.42	4.8
Savannah River, GA	32°31.93'N/ 81°16.58'W	7/12/2006	14:00	27.5	0	6.84	4.3
Cooper River, SC	32°48.79'N/ 79°54.43'W	7/12/2006	18:17	29.1	25	7.80	4.8
Great Pee Dee River, SC	33°39.70'N/ 79°09.19'W	7/12/2006	21:00	26.3	0	6.65	5.2
Cape Fear River, NC	34°13.66'N/ 77°57.01'W	7/13/2006	14:00	28.1	2	6.90	3.8
<i>Salt Marshes</i>							
Hudson Creek, GA	31°27.23'N/ 81°21.77'W	7/11/2006	14:35	28.7	30	7.34	3.4
Sapelo River, GA	31°32.38'N/ 81°25.44'W	7/11/2006	18:00	28.3	29	7.27	3.8

**Table 3. Concentrations of DOC and POC and elemental ratios of dissolved organic matter for 2005 cruises to the SAB.**

Station	Depth (m)	Date	POC (µg/L) <sup>a</sup>	POC standard deviation <sup>a</sup>	DOC (µM) mean	DOC standard deviation <sup>b</sup>	DON (µM) mean	DON error <sup>c</sup>	DOP (µM) mean	DOP error <sup>c</sup>	DOC:DON mean	DOC:DON error <sup>c</sup>
<i>March 2005 cruise</i>												
A01	2	3/27/05			100	2.79	5.83	0.15	0.02	0.09	17.12	0.64
A01	14	3/27/05			101	0.60	7.29	0.12	0.03	0.04	13.90	0.24
A04	2	3/27/05			82	1.16	5.20	0.27	0.01	0.02	15.74	0.83
A04	30	3/27/05			73	1.70	4.29	0.45	0.00	0.05	17.07	1.84
A08	2	3/27/05			76	0.47	5.28	0.13	0.05	0.07	14.31	0.37
A08	50	3/27/05			77	0.65	4.55	0.72	0.01	0.04	17.02	2.69
A08	150	3/27/05			77	0.21	9.03	0.94	0.41	0.02	8.54	0.89
A08	600	3/27/05			54	3.34	6.89	1.06	0.34	0.08	7.78	1.29
B01	2	3/26/05			125	1.17	6.25	0.66	0.07	0.09	20.10	2.13
B01	15	3/26/05			126	0.34	6.48	0.19	0.10	0.07	19.45	0.58
B07	2	3/26/05	85		79	0.30	5.39	0.40	0.10	0.00	14.62	1.08
B07	15	3/26/05			74	0.02	4.67	0.30	0.12	0.12	15.88	1.02
B07	38	3/26/05			74	1.25	4.86	0.19	0.06	0.05	15.21	0.65
B11	2	3/26/05	19		72	0.95	3.14	0.77	0.05	0.12	24.04	5.89
B11	50	3/26/05			75	1.93	4.52	0.28	0.00	0.03	16.55	1.11
B11	150	3/26/05			72	1.39	5.36	0.31	0.06	0.01	13.38	0.82
B11	300	3/26/05			56	1.29	7.33	0.60	0.31	0.05	7.62	0.64
B11	497	3/26/05			49	0.91	9.31	0.68	0.64	0.08	5.32	0.40
B11	630	3/26/05			48	1.95	9.20	0.50	0.64	0.07	5.26	0.36
C01	2	3/23/05	200	12	167	2.15	7.61	0.60	0.00	0.13	22.02	1.76
C09	2	3/23/05	36		89	0.42	4.97	0.42	0.00	0.00	17.88	1.51
C09	31	3/23/05			87	0.53	4.98	0.34	0.00	0.03	17.41	1.19
C14	2	3/23/05	93	22	79	0.83	4.76	0.33	0.00	0.04	16.66	1.17
C14	50	3/23/05			76	0.12	4.98	0.35	0.00	0.01	15.30	1.09

<sup>a</sup> POC filters were only analyzed for selected stations and not always in duplicate; means and standard deviations are presented for those duplicates analyzed.

<sup>b</sup> Dissolved C, N, and P were analyzed in duplicate and the reported standard deviation represents the error of duplicates.

<sup>c</sup> Errors for DON and DOP are propagated from the individual errors of duplicate analyses in TDN or TDP and their associated nutrients (DIN or DIP). Similar error propagation is represented for elemental ratios.

**Table 3. (cont.)**

Station	Depth (m)	Date	POC ( $\mu\text{g/L}$ )	POC standard deviation	DOC ( $\mu\text{M}$ ) mean	DOC standard deviation	DON ( $\mu\text{M}$ ) mean	DON error	DOP ( $\mu\text{M}$ ) mean	DOP error	DOC:DON mean	DOC:DON error
C14	150	3/23/05			57	0.55	5.95	0.79	0.00	0.04	9.68	1.29
C14	249	3/23/05			77	0.00	5.60	0.73	0.00	0.05	14.05	1.82
D02	2	3/21/05	269		127	0.00	6.08	0.54	0.00	0.10	19.69	1.76
D02	9	3/21/05			113	0.63	6.08	0.22	0.00	0.02	18.49	0.67
D07	2	3/21/05	143		72	0.93	5.33	0.41	0.17	0.01	13.52	1.04
D07	31	3/21/05			70	1.68	5.57	0.32	0.13	0.19	12.58	0.79
D11	2	3/22/05	95		76	2.29	5.13	0.18	0.00	0.04	14.78	0.69
D11	26	3/22/05			69	0.94	5.82	0.38	0.07	0.14	11.79	0.79
D11	50	3/22/05			64	0.11	6.39	0.22	0.03	0.15	10.08	0.35
D11	150	3/22/05			51	1.68	9.59	0.65	0.30	0.06	5.30	0.40
D11	298	3/22/05			45	0.61	13.40	0.81	0.57	0.01	3.38	0.21
D11	381	3/22/05	6		47	2.92	13.85	0.68	0.29	0.10	3.39	0.27
E01	2	3/20/05			127	1.07	6.69	0.84	0.21	0.15	19.20	2.41
E01	12	3/20/05			126	0.00	6.04	0.11	0.21	0.01	21.09	0.37
E07	2	3/20/05			75	0.48	2.18	0.16	0.10	0.06	34.33	2.57
E07	11	3/20/05			76	0.00	2.35	0.75	0.17	0.04	46.25	14.66
E07	30	3/20/05			77	0.96	3.91	0.36	0.11	0.02	19.68	1.85
E11	2	3/20/05			80	0.94	4.64	0.10	0.22	0.11	17.15	0.41
E11	50	3/20/05			74	0.00	5.53	0.40	0.26	0.10	12.48	0.90
E11	150	3/20/05			56	0.00	6.46	0.68	0.15	0.08	8.87	0.94
E11	300	3/20/05			57	0.31	6.31	1.34	0.39	0.04	9.10	1.93
E12	2	3/21/05	25		80	0.21	2.14	1.86	0.01	0.05	24.22	21.03
E12	50	3/21/05			80	0.00	3.91	0.16	0.12	0.19	20.12	0.82
E12	100	3/21/05			81	5.95	4.22	0.32	0.00	0.00	19.30	2.02
E12	150	3/21/05			73	0.00	3.68	0.14	0.02	0.06	19.90	0.76
E12	500	3/21/05			59	0.09	5.40	0.94	0.09	0.03	11.08	1.93
E12	900	3/21/05	4		53	0.51	10.53	1.36	0.40	0.20	5.01	0.65
<i>July/August 2005 cruise</i>												
A01	2	8/3/05			92	0.00	7.26	0.44	0.04	0.10	12.44	0.75



**Table 3. (cont.)**

Station	Depth (m)	Date	POC (µg/L)	POC standard deviation	DOC (µM) mean	DOC standard deviation	DON (µM) mean	DON error	DOP (µM) mean	DOP error	DOC:DON mean	DOC:DON error
A01	12	8/3/05			100	0.00	7.60	0.32	0.06	0.11	13.05	0.55
A04	2	8/3/05			90	0.00	5.92	0.13	0.00	0.07	14.86	0.32
A04	31	8/3/05			86	0.00	6.71	0.26	0.11	0.09	12.71	0.50
A08	1	8/3/05			85	0.00	6.02	0.35	0.00	0.04	14.01	0.81
A08	50	8/3/05			80	0.00	5.65	0.29	0.02	0.12	14.03	0.72
A08	150	8/3/05			65	0.00	5.84	0.14	0.00	0.06	11.03	0.26
A08	302	8/3/05			54	0.00	6.26	0.40	0.00	0.09	8.53	0.55
A08	499	8/3/05			58	0.00	5.38	1.09	0.00	0.18	10.00	2.03
A08	693	8/3/05			50	0.00	5.88	0.43	0.00	0.08	8.86	0.65
B01	2	8/2/05			89	2.23	8.09	0.52	0.03	0.05	10.94	0.75
B01	15	8/2/05			91	3.52	8.39	0.76	0.09	0.16	10.86	1.06
B07	2	8/2/05			77	0.05	7.07	0.71	0.14	0.02	10.92	1.10
B07	37	8/2/05			74	0.04	6.72	0.15	0.08	0.09	11.08	0.25
B11	1	8/2/05			82	6.64	6.18	0.10	0.03	0.07	13.32	1.10
B11	50	8/2/05			75	4.15	6.41	0.08	0.10	0.05	11.64	0.66
B11	150	8/2/05			52	0.00	5.44	0.49	0.00	0.06	9.58	0.87
B11	300	8/2/05			48	1.65	4.48	0.19	0.03	0.10	10.69	0.58
B11	501	8/2/05			43	0.04	3.41	0.68	0.03	0.07	12.58	2.50
B11	640	8/2/05			47	3.42	4.34	0.28	0.10	0.10	10.72	1.05
C01	2	7/30/05	505	153	232	0.40	14.89	0.70	0.30	0.10	15.58	0.74
C09	2	7/30/05	38		100	1.39	7.49	0.22	0.04	0.09	13.39	0.44
C09	34	7/30/05			87	1.14	7.12	0.29	0.18	0.06	12.29	0.53
C15	1	7/30/05	25		82	0.66	5.93	0.14	0.00	0.08	13.78	0.35
C15	50	7/30/05			84	2.41	6.18	0.15	0.00	0.09	13.56	0.51
C15	151	7/30/05			62	7.43	4.27	0.24	0.06	0.10	14.46	1.91
C15	300	7/30/05			66		3.54	1.53	0.00	0.13	14.01	6.06
C15	454	7/30/05			53	1.54	2.94	0.56	0.00	0.09	18.70	3.58
D02	2	7/29/05			114	2.48	7.99	1.75	0.04	0.08	14.66	3.22
D02	8	7/29/05			116	0.39	8.29	0.25	0.08	0.03	13.99	0.42
D07	2	7/29/05			135	0.16	9.11	0.08	0.04	0.09	14.77	0.13

Table 3. (cont.)

Station	Depth (m)	Date	POC (µg/L)	POC standard deviation	DOC (µM) mean	DOC standard deviation	DON (µM) mean	DON error	DOP (µM) mean	DOP error	DOC:DON mean	DOC:DON error
D07	37	7/29/05	76	3.02	6.55	0.32	0.02	0.05	11.64	0.73		
D11	2	7/29/05	82	0.15	6.30	0.11	0.00	0.08	13.00	0.22		
D11	51	7/29/05	81	0.03	5.67	0.25	0.02	0.12	14.22	0.63		
D11	150	7/29/05	65	3.05	5.48	0.44	0.00	0.05	11.80	1.10		
D11	298	7/29/05	48	0.14	3.12	0.45	0.00	0.02	15.53	2.26		
D11	376	7/29/05	51	0.83	2.64	0.27	0.00	0.05	19.35	1.97		
E01	2	7/28/05	124	0.54	8.25	0.28	0.10	0.06	15.02	0.52		
E01	10	7/28/05	120	2.89	7.66	0.71	0.07	0.03	15.73	1.50		
E07	2	7/28/05	96	0.71	6.02	0.33	0.00	0.03	15.95	0.88		
E07	30	7/28/05	90	2.98	5.66	0.29	0.00	0.08	15.87	0.97		
E11	2	7/28/05	105	0.58	5.94	0.28	0.06	0.07	17.68	0.85		
E11	50	7/28/05	83	2.44	5.33	0.16	0.13	0.06	15.53	0.64		
E11	149	7/28/05	62	2.17	2.44	0.70	0.00	0.07	25.93	7.49		
E11	300	7/28/05	57	0.48	1.60	0.27	0.00	0.08	35.96	6.05		
E11	453	7/28/05	60	2.94	2.15	0.58	0.00	0.03	30.24	8.25		
T07	2	8/4/05	90	1.30	6.06	0.82	0.01	0.10	15.12	2.05		
T07	51	8/4/05	84	0.77	5.76	0.29	0.00	0.07	14.66	0.74		
T07	151	8/4/05	76	0.66	5.26	0.09	0.03	0.14	14.40	0.28		
T07	300	8/4/05	67	2.34	5.04	1.07	0.03	0.09	13.97	3.02		
T07	498	8/4/05	63	0.84	4.45	0.61	0.00	0.04	14.35	1.98		
T07	989	8/4/05	60	1.71	4.54	0.67	0.00	0.01	13.19	1.99		
<i>October 2005 cruise</i>												
A01	1	10/15/05	151	1.77	10.77	0.12	0.10	0.10	14.03	0.22		
A01	11	10/15/05	150	1.42	10.95	0.67	0.07	0.08	13.77	0.85		
A04	1	10/15/05	118	0.28	9.53	0.29	0.06	0.07	12.40	0.38		
A04	29	10/15/05	114	0.44	8.91	0.46	0.23	0.13	12.84	0.67		
A08	1	10/15/05	80	1.00	6.42	0.12	0.00	0.09	12.53	0.29		
A08	50	10/15/05	79	1.62	5.79	0.38	0.08	0.10	13.65	0.94		
A08	150	10/15/05	62	0.63	5.53	0.39	0.00	0.04	11.31	0.81		

**Table 3. (cont.)**

Station	Depth (m)	Date	POC (µg/L)	POC standard deviation	DOC (µM) mean	DOC standard deviation	DON (µM) mean	DON error	DOP (µM) mean	DOP error	DOC:DON mean	DOC:DON error
A08	300	10/15/05			55	0.88	5.56	0.19	0.00	0.05	9.84	0.37
A08	500	10/15/05			51	0.97	6.07	0.80	0.04	0.07	8.59	1.15
A08	760	10/15/05			49	0.67	6.70	0.91	0.01	0.06	7.41	1.01
B01	2	10/14/05	256		200	1.69	12.44	0.52	0.11	0.07	16.06	0.69
B01	14	10/14/05			170	3.00	10.62	0.41	0.08	0.03	16.00	0.68
B07	1	10/14/05	59		86	0.84	7.23	0.35	0.03	0.12	11.85	0.58
B07	36	10/14/05			87	0.22	8.29	0.41	0.05	0.03	10.49	0.51
B11	1	10/15/05	18		83	1.13	5.99	0.10	0.00	0.09	13.91	0.31
B11	50	10/15/05			84	1.68	5.95	0.08	0.00	0.03	14.04	0.33
B11	150	10/15/05			59	1.33	4.90	0.47	0.00	0.02	12.09	1.18
B11	300	10/15/05			54	0.26	5.35	0.32	0.00	0.05	10.04	0.61
B11	500	10/15/05			49	0.37	5.00	1.05	0.01	0.03	9.91	2.08
B11	623	10/15/05			48	0.09	4.80	0.39	0.00	0.04	10.00	0.82
C01	2	10/11/05	644	76	238	0.51	13.44	0.42	0.14	0.04	17.73	0.55
C09	1	10/12/05	82		101	1.93	6.75	0.58	0.03	0.09	15.01	1.31
C09	27	10/12/05			98	0.30	7.37	0.14	0.01	0.03	13.32	0.25
C15	2	10/14/05	23	0	85	1.63	5.69	0.17	0.00	0.02	14.92	0.54
C15	51	10/14/05			83	1.37	5.63	0.32	0.00	0.08	14.81	0.88
C15	150	10/14/05			65	0.99	4.65	0.22	0.00	0.04	13.97	0.70
C15	300	10/14/05			58	2.19	3.40	0.27	0.00	0.05	17.02	1.51
C15	465	10/14/05	5		53	2.51	2.35	0.68	0.00	0.09	22.71	6.64
D02	1	10/10/05	312		128	0.68	8.33	0.81	0.00	0.04	15.47	1.50
D02	8	10/10/05			129	8.19	9.44	0.29	0.02	0.13	13.71	0.97
D07	2	10/10/05	48		90	1.31	6.36	0.17	0.08	0.15	14.23	0.42
D07	39	10/10/05			86	0.28	6.12	0.10	0.04	0.06	14.12	0.23
D11	2	10/10/05	31		86	0.00	6.33	0.49	0.10	0.06	12.85	1.00
D11	52	10/10/05			87	1.11	6.04	0.18	0.02	0.07	14.32	0.46
D11	153	10/10/05			59	0.11	3.65	0.40	0.00	0.03	16.29	1.77
D11	302	10/10/05			61	4.52	2.37	0.69	0.00	0.18	26.10	7.80
D11	393	10/10/05			53	1.25	3.31	0.53	0.00	0.10	15.93	2.56

**Table 3. (cont.)**

Station	Depth (m)	Date	POC (µg/L)	POC standard deviation	DOC (µM) mean	DOC standard deviation	DON (µM) mean	DON error	DOP (µM) mean	DOP error	DOC:DON mean	DOC:DON error
E01	1	10/8/05	131	1.09	9.91	0.20	0.04	0.05	13.25	0.29		
E01	7	10/8/05	131	1.33	8.71	0.22	0.03	0.03	14.99	0.41		
E07	1	10/9/05	80	0.44	5.64	0.22	0.00	0.04	14.20	0.56		
E07	28	10/9/05	78	1.05	5.72	0.25	0.00	0.08	13.70	0.63		
E11	1	10/9/05	76	0.97	5.80	0.28	0.00	0.10	13.15	0.65		
E11	50	10/9/05	70	0.54	5.94	0.42	0.00	0.06	11.73	0.83		
E11	150	10/9/05	52	2.64	3.21	0.76	0.00	0.04	16.24	3.93		
E11	299	10/9/05	49	1.27	3.49	1.36	0.00	0.08	14.21	5.54		
E11	438	10/9/05	48	0.22	2.99	0.26	0.00	0.13	16.01	1.41		
T07a	2	10/16/05	82	4.51	5.56	0.39	0.00	0.04	14.71	1.32		
T07a	50	10/16/05	87	1.87	5.13	0.26	0.02	0.08	17.00	0.93		
T07a	150	10/16/05	81	1.60	5.68	0.27	0.00	0.03	14.27	0.72		
T07a	300	10/16/05	60	0.09	4.71	0.16	0.00	0.11	12.82	0.44		
T07a	500	10/16/05	55	0.10	4.15	0.20	0.00	0.03	13.35	0.66		
T07a	898	10/16/05	51	1.36	3.79	0.08	0.05	0.06	13.54	0.46		

**Table 4. DOC and POC isotopic values for 2005 cruises to the SAB and 2006 river and salt marsh end members.**

Station	Depth (m)	Date	Replicate	$\delta^{13}\text{C-POC}$ (‰)	$\Delta^{14}\text{C-POC}$ (‰)	$\Delta^{14}\text{C-POC age}$ (BP)	$\Delta^{14}\text{C-POC age error}$	$\delta^{13}\text{C-DOC}$ (‰)	$\Delta^{14}\text{C-DOC}$ (‰)	$\Delta^{14}\text{C-DOC age}$ (BP)	$\Delta^{14}\text{C-DOC age error}$
<i>March 2005 cruise</i>											
B01	2	3/26/2005	A					-23.3	-101	801	67
			B					-24.1	-121	987	70
B07	2	3/26/2005	A	-20.4	49	Modern	35	-21.8	-190	1640	90
			B					-21.5	-189	1628	92
B11	2	3/26/2005	A	-22.6	-43	300	44	-22.2	-281	2598	122
			B								
Sapelo R.	2	3/23/2005	A	-21.5	-44	309	35	-24.2	-30	191	107
			B								
C01	2	3/23/2005	A	-22.3	-29	186	35	-24.8	-61	450	53
			B					-24.8	-53	382	109
C09	2	3/23/2005	A	-23.3	22	Modern	36	-22.0	-175	1488	59
			B					-21.7	-183	1576	85
C14	2	3/23/2005	A	-18.5	53	Modern	35	-22.2	-242	2178	69
			B					-21.7	-248	2237	97
D02	2	3/21/2005	A	-21.7	-8	9	34	-24.3	-66	499	70
			B								
D07	2	3/21/2005	A	-20.0	61	Modern	34	-21.5	-215	1895	86
			B					-22.6	-220	1947	93
D11	2	3/22/2005	A	-20.0	49	Modern	33	-22.7	-251	2267	86
			B					-22.9	-244	2193	91
E12	2	3/21/2005	A	-22.2	6	Modern	52	-22.7	-231	2059	85
			B					-19.4 <sup>a</sup>	-252	2277	96
<i>July/August 2005 cruise</i>											
C01	2	7/30/2005	A	-21.2	42	Modern	34	-24.9	-6	Modern	63
			B								
C09	2	7/30/2005	A	-21.5	29	Modern	35	-22.9	-169	1433	93
			B								

<sup>a</sup> Value was considered an outlier and excluded from data analysis

Table 4. (cont.)

Station	Depth (m)	Date	Replicate	$\delta^{13}\text{C-POC}$ (‰)	$\Delta^{14}\text{C-POC}$ (‰)	$\Delta^{14}\text{C-POC age}$ (BP)	$\Delta^{14}\text{C-POC age error}$	$\delta^{13}\text{C-DOC}$ (‰)	$\Delta^{14}\text{C-DOC}$ (‰)	$\Delta^{14}\text{C-DOC age}$ (BP)	$\Delta^{14}\text{C-DOC age error}$
C15	1	7/30/2005	A	-20.0	12	Modern	44	-22.9	-241	2163	99
			B					-21.8	-243	2183	87
<i>October 2005 cruise</i>											
B01	2	10/14/2005	A	-21.3	-3	Modern	36	-24.0	54	Modern	76
			B					-24.8	50	Modern	63
B07	1	10/14/2005	A	-22.1	-16	80	33	-22.5	-120	976	100
			B					-21.4	-87	681	85
B11	1	10/15/2005	A	-21.5	-51	370	58	-21.4	-133	1091	88
			B								
C01	2	10/11/2005	A	-20.7	-43	301	36	-23.0	41	Modern	60
			B								
C09	1	10/12/2005	A	-21.6	2	Modern	37	-22.4	-103	824	116
			B								
C15	2	10/14/2005	A	-21.3	-73	556	52	-21.0	-135	1115	91
			B								
D02	1	10/10/2005	A	-20.5	-33	217	47	-23.0	-118	958	74
			B								
D07	2	10/10/2005	A	-21.6	-5	Modern	34	-21.8	-221	1956	82
			B								
D11	2	10/10/2005	A	-21.5	-31	197	43	-22.0	-248	2240	102
			B								
<i>Deep Outer Shelf/Slope</i>											
D11	381	3/22/2005	A	-24.4	-248	2240	159	-21.6	-390	3922	131
			B								
E12	900	3/21/2005	A	-28.2	-479	5187	132	-22.9	-392	3942	71
			B								
C15	465	10/14/2005	A	-27.3	-458	4866	162	-22.0	-373	3703	178
			B					-21.5	-359	3514	236

**Table 4. (cont.)**

Station	Depth (m)	Date	Replicate	$\delta^{13}\text{C}$ -POC (‰)	$\Delta^{14}\text{C}$ -POC (‰)	$\Delta^{14}\text{C}$ -POC age (BP)	$\Delta^{14}\text{C}$ -POC age error	$\delta^{13}\text{C}$ -DOC (‰)	$\Delta^{14}\text{C}$ -DOC (‰)	$\Delta^{14}\text{C}$ -DOC age (BP)	$\Delta^{14}\text{C}$ -DOC age error
<i>Salt Marsh Creeks</i>											
Hudson Creek, GA		7/11/2006	A	-22.9	-321 <sup>a</sup>	3060	41	-20.4	-38	257	35
			B								
Sapelo River, GA		7/11/2006	A	-24.4	11	Modern	36	-22.7	34	Modern	33
			B	-24.7	-13	56	34	-20.5	-3	Modern	34
<i>Rivers (S&lt;3)</i>											
Altamaha River, GA		7/11/2006	A	-27.6	-58	429	36	-28.3	45	Modern	34
			B								
Savannah River, GA		7/12/2006	A	-32.1	-11	38	43	-28.5	63	Modern	41
			B	-32.2	-19	98	37				
Great Pee Dee River, SC		7/12/2006	A	-30.6	-16	74	53	-28.2	100	Modern	33
			B								

<sup>a</sup> Value was considered an outlier and excluded from data analysis

**Table 5. DIC concentrations and isotopic values for 2005 cruises to the SAB and 2006 river and salt marsh end members.**

Station <sup>a</sup>	Sample Depth (m)	Date	Bottle	DIC (μM)	δ <sup>13</sup> C-DIC (‰)	Δ <sup>14</sup> C-DIC (‰)	Δ <sup>14</sup> C-DIC age (BP)	Δ <sup>14</sup> C-DIC age error
<i>March 2005 cruise</i>								
B01	2	3/26/2005	A	2097	0.4	54	Modern	38
		3/26/2005	B					
B01	15	3/26/2005	A					
		3/26/2005	B	2101	0.5	54	Modern	33
B07	2	3/26/2005	A	2114	0.8	64	Modern	34
		3/26/2005	B	2118	0.9	66	Modern	34
B07	15	3/26/2005	A	2136	0.6			
		3/26/2005	B					
B07	38	3/26/2005	A					
		3/26/2005	B	2055	0.9	70	Modern	33
B11	2	3/26/2005	A	2117	-0.2			
		3/26/2005	B	2119	0.9			
B11	50	3/26/2005	A	2112	0.8			
		3/26/2005	B	2111	1.0			
B11	150	3/26/2005	A	2176	0.6			
		3/26/2005	B					
B11	300	3/26/2005	A	2217	0.5			
		3/26/2005	B					
B11	497	3/26/2005	A	2269	0.3			
		3/26/2005	B					
B11	630	3/26/2005	A	2260	0.6			
		3/26/2005	B	2264	0.5			
<i>Altamaha R.</i>	2	3/22/2005	A	1938	0.5			
		3/22/2005	B	1938				
<i>Sapelo R.</i>	2	3/23/2005	A	1960	-0.6	61	Modern	37
		3/23/2005	B	1960	-0.4	71	Modern	48
Č01	2	3/23/2005	A	1956	-0.2	60	Modern	42

<sup>a</sup> Stations in italic font were sampled only for DIC isotopes and DOC concentrations.



**Table 5. (cont.)**

Station	Sample Depth (m)	Date	Bottle	DIC ( $\mu\text{M}$ )	$\delta^{13}\text{C-DIC}$ (‰)	$\Delta^{14}\text{C-DIC}$ (‰)	$\Delta^{14}\text{C-DIC}$ age (BP)	$\Delta^{14}\text{C-DIC}$ age error
C01	2	3/23/2005	B	2006	-0.3	57	Modern	57
C03	2	3/23/2005	A	2012	-0.1			
C04	2	3/23/2005	A	2064	0.3			
C05	2	3/23/2005	A	2095	0.4	56	Modern	45
C05	19	3/23/2005	A	2102	0.1	60	Modern	43
C07	2	3/23/2005	A	2122				
C07	22	3/23/2005	A	2138	0.4			
C09	2	3/23/2005	A	2107		64	Modern	43
			B	2135	0.7	73	Modern	48
C09	25	3/23/2005	A	2129	0.5			
			B	2131	0.7	68	Modern	42
C11	2	3/23/2005	A	2115	1.0			
C11	38	3/23/2005	A	2127	1.0			
C12	2	3/23/2005	A	2119	1.0			
C12	46	3/23/2005	A	2124	0.6			
C13	2	3/23/2005	A	2095	0.8			
C13	71	3/23/2005	A	2121				
C14	2	3/23/2005	A	2073	1.3	85	Modern	42
			B	2070	1.3	48	Modern	42
C14	50	3/23/2005	A	2116	1.1	66	Modern	42
			B	2111	1.0	94	Modern	42
C14	150	3/23/2005	A	2196	0.7	78	Modern	37
			B	2210	0.7	63	Modern	42
C14	249	3/23/2005	A	2180	0.7	63	Modern	46
			B	2141	0.8	73	Modern	41
C15	2	3/23/2005	A	2065	1.2	70	Modern	46
C15	51	3/23/2005	A	2121	0.7	69	Modern	33
C15	150	3/23/2005	A	2161	0.6	74	Modern	41
C15	459	3/23/2005	A	2253	0.7	-52	377	48
C16	2	3/23/2005	A	2064	1.3	67	Modern	33

**Table 5. (cont.)**

Station	Sample Depth (m)	Date	Bottle	DIC ( $\mu\text{M}$ )	$\delta^{13}\text{C-DIC}$ (‰)	$\Delta^{14}\text{C-DIC}$ (‰)	$\Delta^{14}\text{C-DIC}$ age (BP)	$\Delta^{14}\text{C-DIC}$ age error
C16	50	3/23/2005	A	2064	1.3	69	Modern	43
C16	150	3/23/2005	A	2149	0.7	81	Modern	40
C16	500	3/23/2005	A	2226	0.6	22	Modern	43
C16	765	3/23/2005	A	2252	0.4	-58	428	43
D02	2	3/21/2005	A	1986	0.2	62	Modern	33
		3/21/2005	B					
D02	9	3/21/2005	A	2036	0.9	62	Modern	33
		3/21/2005	B	2031	0.8	59	Modern	33
D07	2	3/21/2005	A	2119	0.9	68	Modern	34
		3/21/2005	B					
D07	31	3/21/2005	A					
		3/21/2005	B	2114	0.9	70	Modern	33
D11	2	3/22/2005	A	2087	0.8			
		3/22/2005	B	2082	0.8			
D11	50	3/22/2005	A	2144	0.8			
		3/22/2005	B					
D11	150	3/22/2005	A	2214	0.6			
		3/22/2005	B					
D11	381	3/22/2005	A					
		3/22/2005	B	2246				
<i>July/August 2005 cruise</i>								
B01	2	8/2/2005	A	2118	1.1			
		8/2/2005	B	2118	1.0			
B01	15	8/2/2005	A	2140	0.8			
		8/2/2005	B					
B07	2	8/2/2005	A	2096				
		8/2/2005	B					
B07	37	8/2/2005	A	2139	1.3			
		8/2/2005	B					
B11	1	8/2/2005	A	2077	1.3			

Table 5. (cont.)

Station	Sample Depth (m)	Date	Bottle	DIC ( $\mu\text{M}$ )	$\delta^{13}\text{C-DIC}$ (‰)	$\Delta^{14}\text{C-DIC}$ (‰)	$\Delta^{14}\text{C-DIC}$ age (BP)	$\Delta^{14}\text{C-DIC}$ age error
B11	1	8/2/2005	B	2070	1.3			
B11	150	8/2/2005	A	2226	0.7			
		8/2/2005	B					
B11	640	8/2/2005	A	2293	0.7			
		8/2/2005	B					
<i>Sapelo R. 1</i>	1	7/30/2005	A	2061	-2.2	53	Modern	33
<i>Sapelo R. 2</i>	1	7/30/2005	A	2074	-1.8	65	Modern	40
C01	2	7/30/2005	A	2017	-0.7	56	Modern	33
		7/30/2005	B	2026	-0.3	55	Modern	34
C03	2	7/30/2005	A	2048	0.8			
C05	2	7/30/2005	A	2012	1.1	67	Modern	41
C07	2	7/30/2005	A	2053	1.3			
C07	21	7/30/2005	A	2085	1.5			
C09	2	7/30/2005	A	2064	1.3	85	Modern	36
		7/30/2005	B	2064	1.4	74	Modern	42
C09	34	7/30/2005	A	2096	1.5	76	Modern	40
		7/30/2005	B	2102	1.4	80	Modern	41
C11	2	7/30/2005	A	2039	1.7			
C11	36	7/30/2005	A	2060	1.7			
C13	2	7/30/2005	A	2043	1.8			
C13	46	7/30/2005	A	2194	0.8			
C15	1	7/30/2005	A	2025	1.7	86	Modern	405
		7/30/2005	B	2035	1.8	79	Modern	44
C15	50	7/30/2005	A	2094	1.5	70	Modern	40
		7/30/2005	B	2096	1.6	79	Modern	41
C15	151	7/30/2005	A	2218	1.0	21	Modern	42
		7/30/2005	B	2217	1.2	32	Modern	40
C15	300	7/30/2005	A	2385	1.0	-47	336	44
		7/30/2005	B	2237	1.1	-40	277	42
C15	454	7/30/2005	A		1.0	-66	497	43

Table 5. (cont.)

Station	Sample Depth (m)	Date	Bottle	DIC ( $\mu\text{M}$ )	$\delta^{13}\text{C-DIC}$ (‰)	$\Delta^{14}\text{C-DIC}$ (‰)	$\Delta^{14}\text{C-DIC}$ age (BP)	$\Delta^{14}\text{C-DIC}$ age error
C15	454	7/30/2005	B	2224	1.2			
C16	2	7/31/2005	A	2015	1.7	64	Modern	41
C16	52	7/31/2005	A	2047	1.8	58	Modern	40
C16	150	7/31/2005	A	2176	1.2	87	Modern	40
C16	301	7/31/2005	A	2157	1.2	82	Modern	40
C16	497	7/31/2005	A	2238	1.1	-33	221	41
C16	761	7/31/2005	A	2249	1.1	-74	567	42
D02	2	7/29/2005	A	2073	0.9			
		7/29/2005	B					
D02	8	7/29/2005	A	2086	1.0			
D07	2	7/29/2005	B	2038	0.6			
D07	37	7/29/2005	A	2159	0.9			
		7/29/2005	B					
D11	2	7/29/2005	A	2059	0.6			
		7/29/2005	B					
D11	150	7/29/2005	A	2200	0.7			
		7/29/2005	B					
D11	376	7/29/2005	A	2264	0.7			
		7/29/2005	B	2264	0.8			
<i>October 2005 cruise</i>								
B01	2	10/14/2005	A	2003	-0.6			
			B	1834	-0.6	74	Modern	30
B01	14	10/14/2005	A	2026	-0.4	56	Modern	32
			B	2061	-0.3	55	Modern	32
B07	1	10/14/2005	A	2099	1.0	67	Modern	33
			B					
B07	36	10/14/2005	A	2079	1.0	70	Modern	31
			B					

**Table 5. (cont.)**

Station	Sample Depth (m)	Date	Bottle	DIC ( $\mu\text{M}$ )	$\delta^{13}\text{C-DIC}$ (‰)	$\Delta^{14}\text{C-DIC}$ (‰)	$\Delta^{14}\text{C-DIC}$ age (BP)	$\Delta^{14}\text{C-DIC}$ age error
B11	1	10/15/2005	A	2085	1.3			
			B					
B11	150	10/15/2005	A	2216	0.8			
			B					
B11	623	10/15/2005	A	2285	0.8			
			B					
<i>Sapelo R.</i>								
C01	3	10/11/2005	A	1973	-2.1	60	Modern	33
	2	10/11/2005	A	1951	-0.8	67	Modern	42
			B	1955	-0.8	61	Modern	34
C03	1	10/11/2005	A	1941	0.1			
C05	2	10/11/2005	A	1993	0.7	64	Modern	30
C07	2	10/12/2005	A	2000	1.2			
C07	19	10/12/2005	A	1999	1.1			
C09	1	10/12/2005	A	2006	1.3	69	Modern	33
			B	2008	1.3	70	Modern	33
C09	27	10/12/2005	A	2015	1.3	73	Modern	32
			B	2013	1.2	66	Modern	32
C11	1	10/13/2005	A	2024	1.3			
C11	36	10/13/2005	A	2024	1.3			
C13	6	10/13/2005	A	2031	0.8	83	Modern	36
C13	43	10/13/2005	A	2019	1.3	66	Modern	32
C15	2	10/14/2005	A	2016	1.6	66	Modern	32
			B	2017	1.7	70	Modern	32
C15	51	10/14/2005	A	2054	1.4	70	Modern	32
			B	2058	1.5	68	Modern	32
C15	150	10/14/2005	A	2173	1.2			
			B	2173	1.3			
C15	300	10/14/2005	A	2219	1.1			
			B	2220	1.0			
C15	465	10/14/2005	A	2250	0.9			

**Table 5. (cont.)**

Station	Sample Depth (m)	Date	Bottle	DIC ( $\mu\text{M}$ )	$\delta^{13}\text{C-DIC}$ (‰)	$\Delta^{14}\text{C-DIC}$ (‰)	$\Delta^{14}\text{C-DIC}$ age (BP)	$\Delta^{14}\text{C-DIC}$ age error
C15	465	10/14/2005	B	2253	0.9			
C16	2	10/13/2005	A	2004	1.6	70	Modern	32
C16	51	10/13/2005	A	2076	1.4	73	Modern	32
C16	150	10/13/2005	A	2165	1.3			
C16	300	10/13/2005	A	2141	1.2			
C16	500	10/13/2005	A	2177	1.0			
C16	780	10/13/2005	A	2253	0.9			
D02	1	10/10/2005	A	1984	0.2	65	Modern	31
D02	8	10/10/2005	B	2034	0.1	54	Modern	32
D07	2	10/10/2005	A	2058	1.2	68	Modern	32
D07	39	10/10/2005	B	2076	1.1	67	Modern	32
D11	2	10/10/2005	A	2077	1.2	68	Modern	31
D11	153	10/10/2005	B	2072	1.2			
D11	393	10/10/2005	A	2238	0.7			
D11		10/10/2005	B	2273	0.8			
<b>Salt Marsh Creeks</b>								
Hudson Creek, GA	0	7/11/2006	A	2360	-3.0	20	Modern	31
			B	2342	-3.1	33	Modern	32
Sapelo River, GA	0	7/11/2006	A	2764	-3.8	31	Modern	32
			B					
<b>Fresh Water Rivers</b>								
Savannah River, GA	0	7/12/2006	A	537	-11.1	-27	170	32
			B					
Great Pee Dee River, SC	0	7/12/2006	A	441	-14.8	-70	529	32

**Table 5. (cont.)**

Station	Sample Depth (m)	Date	Bottle	DIC ( $\mu\text{M}$ )	$\delta^{13}\text{C-DIC}$ (‰)	$\Delta^{14}\text{C-DIC}$ (‰)	$\Delta^{14}\text{C-DIC}$ age (BP)	$\Delta^{14}\text{C-DIC}$ age error
Great Pee Dee River, SC	0	7/12/2006	B	431		-72	550	38
Cape Fear River, NC	0	7/13/2006	A	580	-11.9	-1	Modern	32
			B					
<i>Estuarine Rivers</i>								
St Johns River, FL	0	7/11/2006	A	1330	-5.1	-37	248	35
			B					
Altamaha River, GA	0	7/11/2006	A	1241	-2.4	-70	530	32
			B					
Cooper River, SC	0	7/12/2006	A	1960	-2.4	-37	250	33
			B					
<i>Gulf Stream</i>								
E12	900	3/21/2005	A	2251	1.0	-29	185	32
			B					
T07	989	8/4/2005	A	2262	1.0	-28	179	32
			B					
T07a	898	10/16/2005	A	2272	1.0	-38	258	32
			B					

**Table 6. DOM dark decomposition results for SAB surface waters.**

	<b>March</b>	<b>July</b>	<b>October</b>
incubation duration (days)	152	289	216
<b>DOC Decay Coefficients, k (day<sup>-1</sup>)<sup>a</sup></b>			
Inner Shelf A	0.00049	0.00033*	0.00085*
Inner Shelf B	-	0.00032	0.00085*
Mid Shelf A	0.00123*	-	0.00065
Mid Shelf B	0.00065	-	0.00065
Outer Shelf A	0.00127*	-	-0.00442*
Outer Shelf B	0.00110*	-	-0.00518*
<b>Fraction of DOC Utilized</b>	<b>March</b>	<b>July</b>	<b>October</b>
Inner Shelf A	0.21	0.09	0.17
Inner Shelf B	-	0.12	0.22
Mid Shelf A	0.11	-	0.12
Mid Shelf B	0.08	-	0.17
Outer Shelf A	0.15	-	-1.46
Outer Shelf B	0.12	-	-1.68
<b>Fraction of DON Utilized</b>	<b>March</b>	<b>July</b>	<b>October</b>
Inner Shelf A	ns <sup>b</sup>	0.56	0.41
Inner Shelf B	ns	0.58	0.44
Mid Shelf A	ns	0.66	0.61
Mid Shelf B	ns	0.73	0.73
Outer Shelf A	ns	0.73	0.39
Outer Shelf B	ns	0.61	0.43

<sup>a</sup> Decay rate coefficients (k) were calculated as a first order reaction.

\* P<0.01 for decay rate coefficients.

<sup>b</sup> ns- no sample



**Table 7. Dual carbon isotope mass balance results for 2005 cruises to the SAB (see text for details). Values represent fractions of the different end members contributing to each sample type and location.**

	DOC			Phytoplankton <sup>a</sup>	DIC Seawater CO <sub>2</sub> <sup>c</sup>	Gulf Stream	Salt Marsh Creeks	Gulf Stream
	River	Gulf Stream	Salt Marsh Creeks					
<i>March Cruise</i>								
inner shelf stations	0.26 to 0.48	0.15 to 0.39	0.25 to 0.44		0.23 to 0.46	0.56 to 0.66		0 to 0.16
mid- and outer shelf stations	0.07 to 0.20	0.54 to 0.78		0.10 to 0.33	0.04 to 0.20	0.66 to 0.95		0 to 0.30
<i>July Cruise</i>								
inner shelf stations	0.51	0.11	0.38		0.40 to 0.49	0.50 to 0.53		0.01 to 0.07
mid- and outer shelf stations	0.09 to 0.26	0.53 to 0.70		0.11 to 0.22	0 to 0.09	0.87 to 0.99		0 to 0.07
<i>October Cruise</i>								
inner shelf stations	0.21 to 0.51	0 to 0.35	0.44 to 0.80		0.30 to 0.52	0.53 to 0.66		0 to 0.03
mid- and outer shelf stations	0.09 to 0.26	0.35 to 0.71		0.19 to 0.49	0 to 0.13	0.77 to 0.87		0.10 to 0.18
	POC			Phytoplankton <sup>a</sup>	DIC Seawater CO <sub>2</sub> <sup>c</sup>	Gulf Stream	Salt Marsh Creeks	Gulf Stream
	Terrestrial <sup>b</sup>	Phytoplankton <sup>a</sup>	Gulf Stream					
<i>March Cruise</i>								
inner shelf stations	0.13 to 0.28	0.58 to 0.66	0.12 to 0.22		0.23 to 0.46	0.56 to 0.66		0 to 0.16
mid- and outer shelf stations	0 to 0.51	0.49 to 1.0	0 to 0.19		0.04 to 0.20	0.66 to 0.95		0 to 0.30
<i>July Cruise</i>								
inner shelf stations	0.28 to 0.29	0.68 to 0.72	0 to 0.03		0.40 to 0.49	0.50 to 0.53		0.01 to 0.07
mid- and outer shelf stations	0.06 to 0.26	0.69 to 0.83	0.05 to 0.11		0 to 0.09	0.87 to 0.99		0 to 0.07
<i>October Cruise</i>								
inner shelf stations	0.02 to 0.19	0.69 to 0.77	0.12 to 0.23		0.30 to 0.52	0.53 to 0.66		0 to 0.03
mid- and outer shelf stations	0.03 to 0.27	0.59 to 0.67	0.10 to 0.37		0 to 0.13	0.77 to 0.87		0.10 to 0.18

<sup>a</sup> Values were estimated from DIC isotopic signatures after correcting for <sup>13</sup>C isotope fractionation (-19‰) by phytoplankton.

<sup>b</sup> Terrestrial source is an average of riverine and salt marsh creek source materials.

<sup>c</sup> Source was based on an average of outer shelf surface DIC isotopic signatures.

**Table 8.  $\Delta^{14}\text{C}$ -DOC isotopic mass balance results for DOM dark decomposition experiments, October 2005.**

<b>Site</b>	<b>Initial <math>\Delta^{14}\text{C}</math>-DOC (‰)</b>	<b>Final <math>\Delta^{14}\text{C}</math>-DOC (‰)</b>	<b><math>\Delta^{14}\text{C}</math>-DOC (‰) of fraction utilized</b>
Inner Shelf A	41 ± 8	-52 ± 7	475 ± 11
Inner Shelf B	41 ± 8	-40 ± 7	334 ± 11
Mid Shelf A	-103 ± 13	-284 ± 8	1319 ± 15
Mid Shelf B	-103 ± 13	-256 ± 8	738 ± 15

Figure 1. Bathymetric map of the South Atlantic Bight (from Menzel 1993).

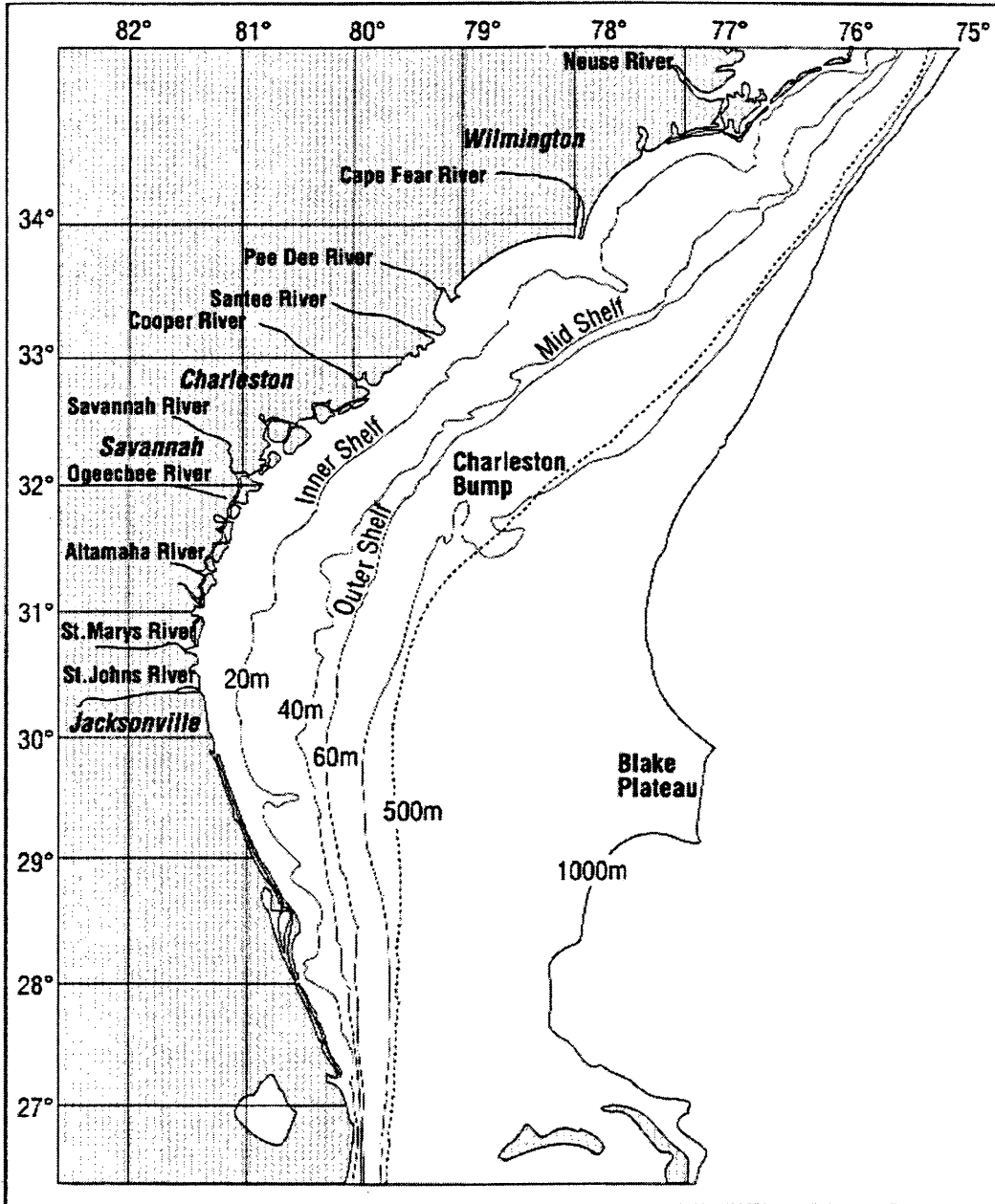


Figure 2. Metabolic balance in the nearshore SAB (from Hopkinson 1985).

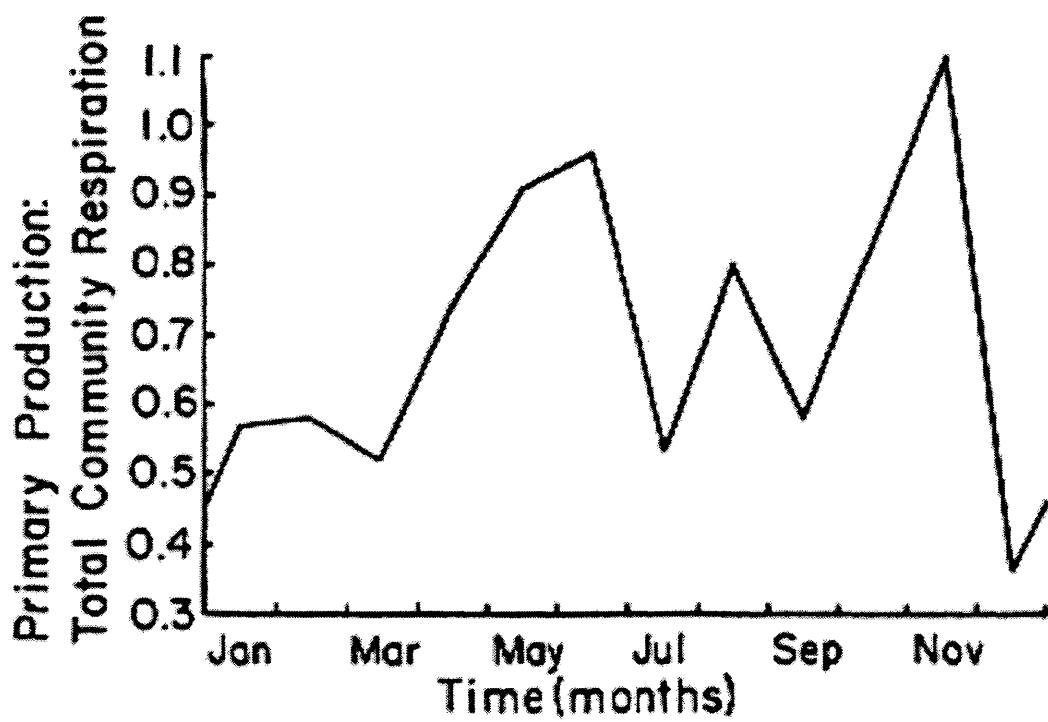


Figure 3.  $p\text{CO}_2$  distributions along transect C in 2000 and 2002 in the SAB (from Cai et al. 2003).

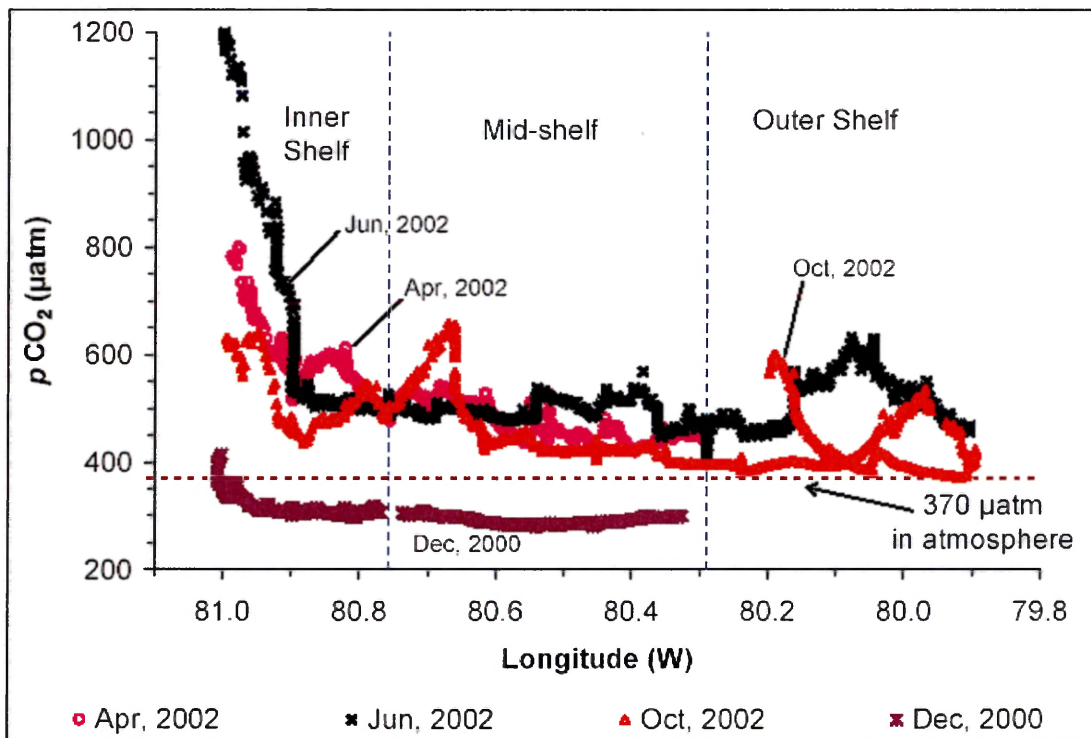




Figure 4. Locations of sampling transects and stations for the March, July and October 2005 cruises to the SAB.

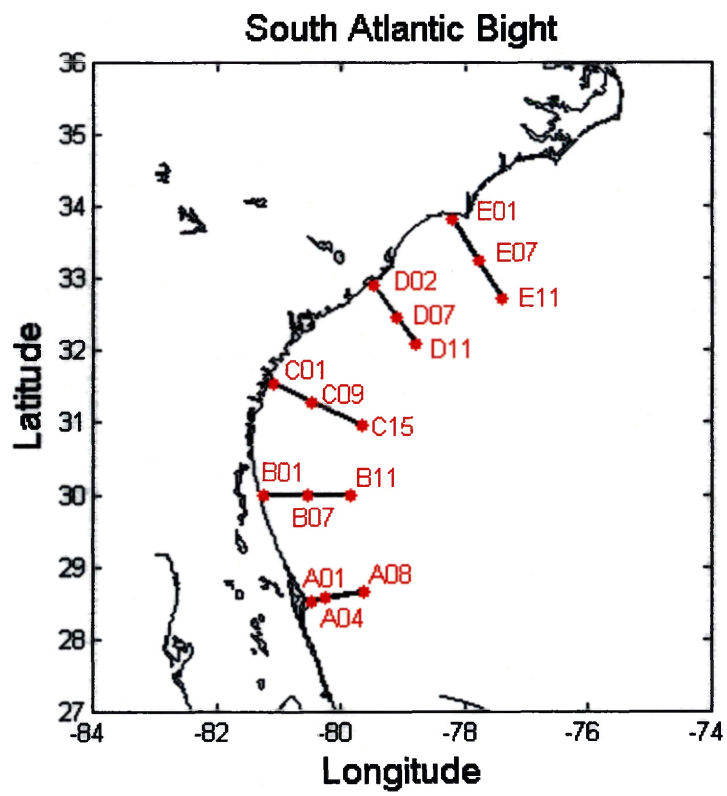


Figure 5. USGS graphs of river discharge (<http://www.usgs.gov/>) for selected rivers (representing the largest inputs to the SAB) discharging to the SAB for 2005-2006: A) Altamaha River, B) Savannah River, C) Pee Dee River, D) Cooper River. Approximate cruise and end member sample trip dates are highlighted in yellow.

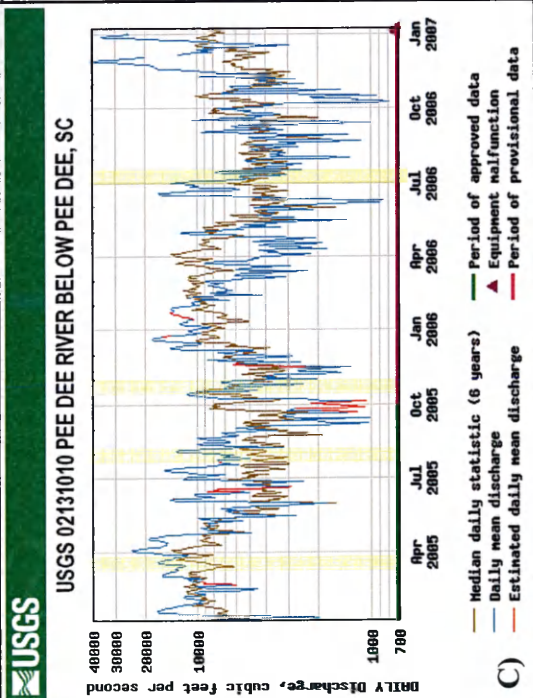
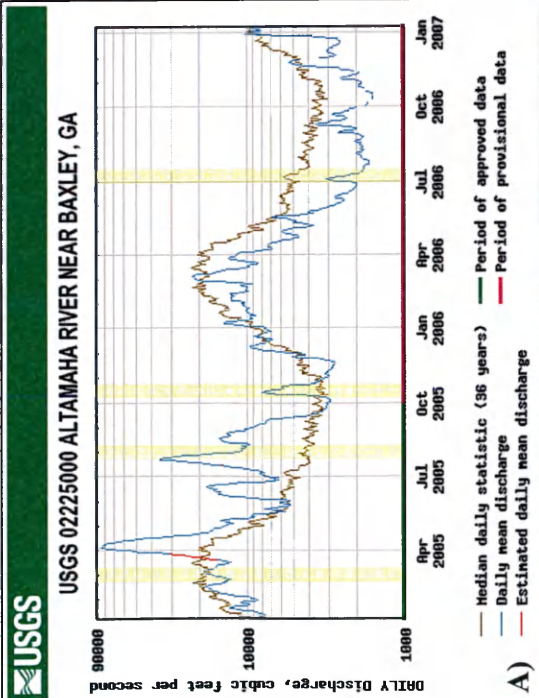
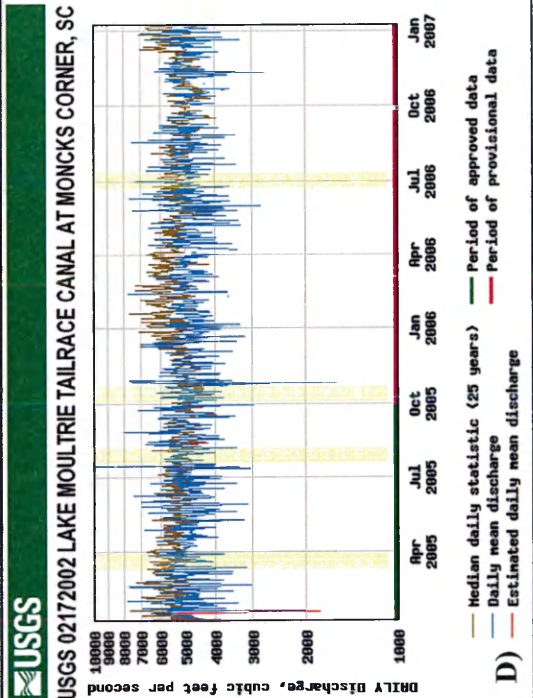
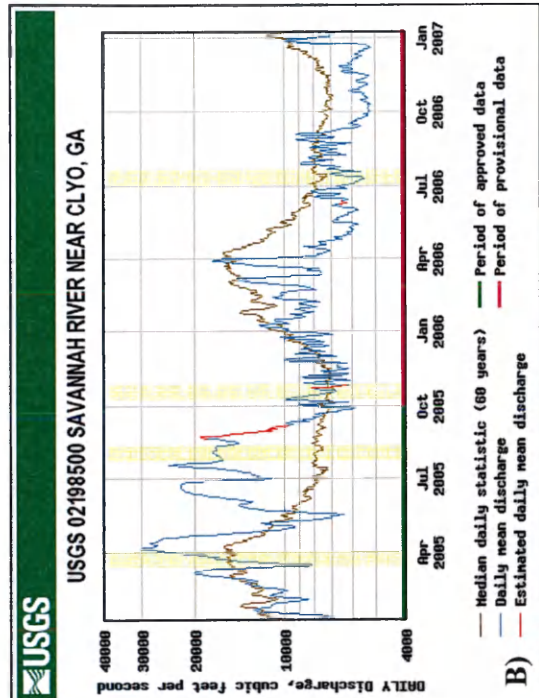


Figure 6. Surface DOC concentrations for A) March, B) July, and C) October 2005 cruises to the SAB. Note different scales for each panel.

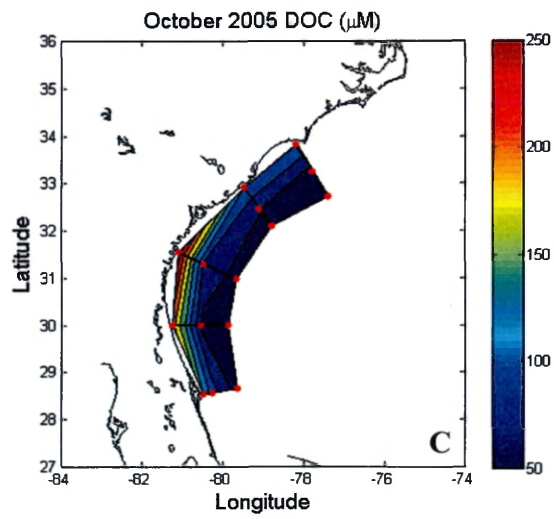
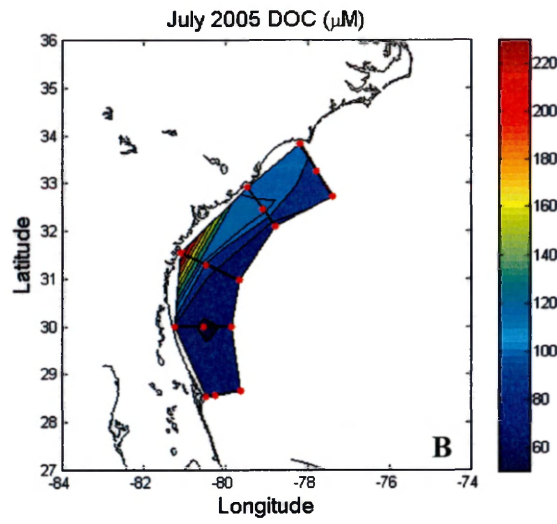
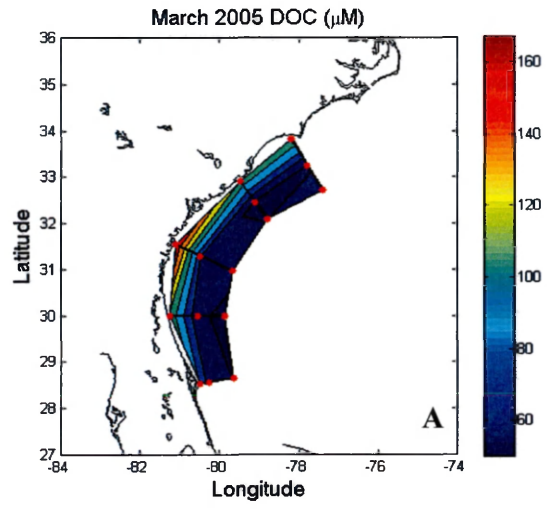


Figure 7. DOC depth profiles for A) March, B) July, and C) October 2005 cruises to the SAB. Error bars represent the standard deviation of duplicate bottles analyzed.

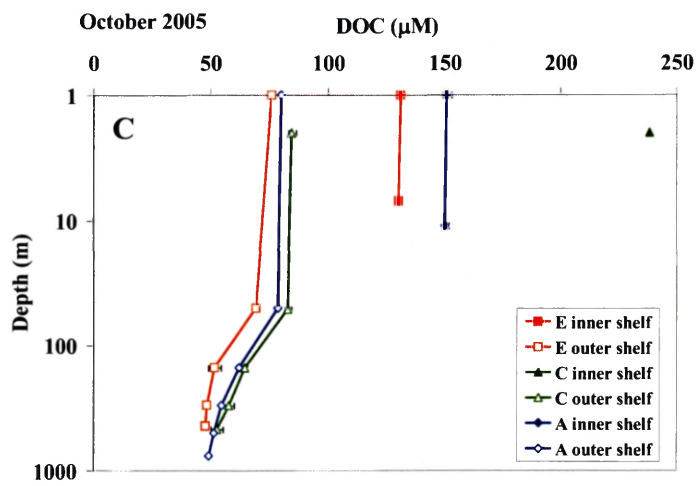
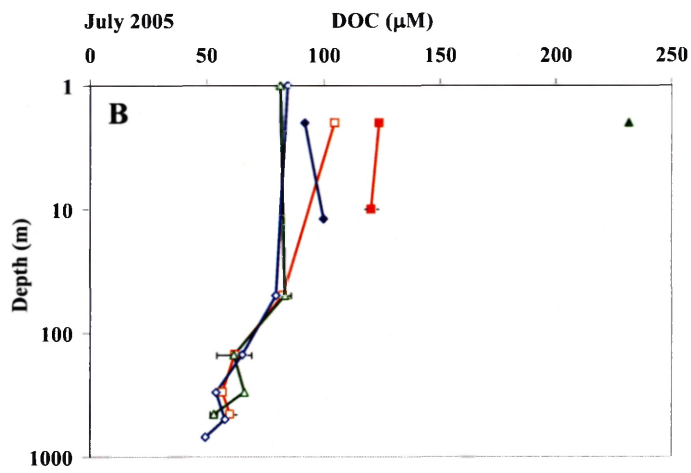
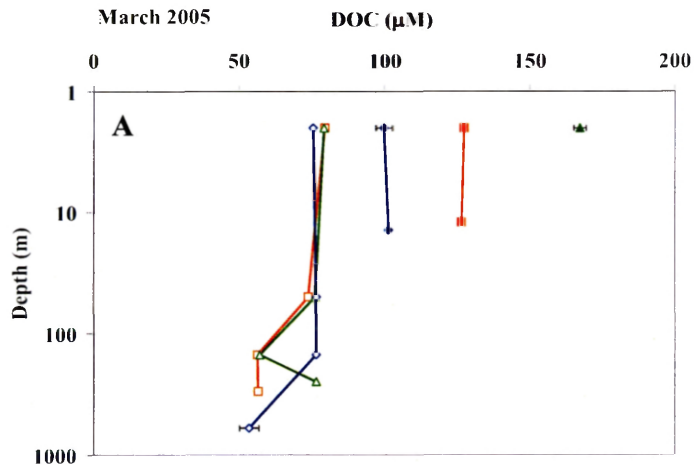




Figure 8. Surface POC concentrations for A) March, B) July, and C) October 2005 cruises to the SAB. In July 2005, only three stations along C transect were selected for POC analysis and results were not contoured. Note different scales for each panel.

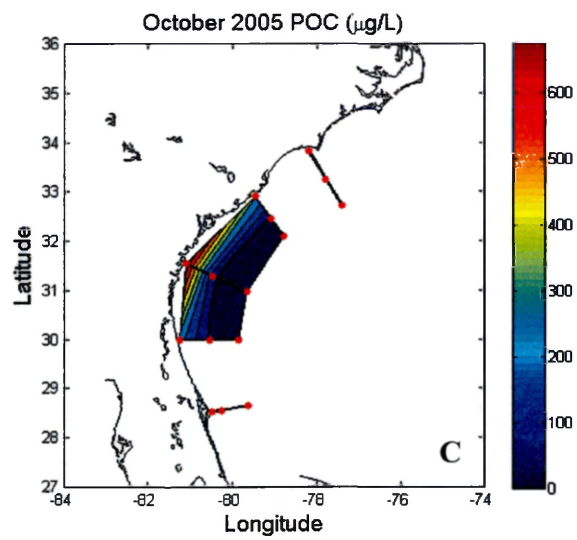
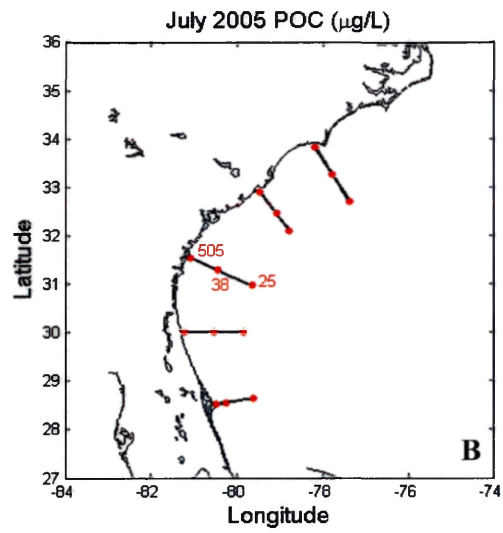
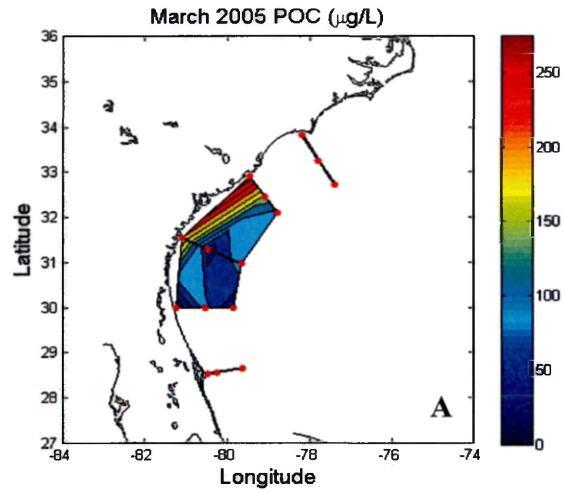


Figure 9. Surface  $\delta^{13}\text{C}$ -DOC distributions for A) March, B) July, and C) October 2005 cruises to the SAB.

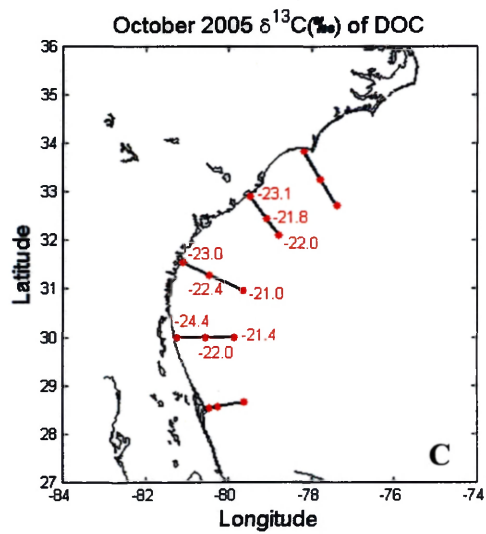
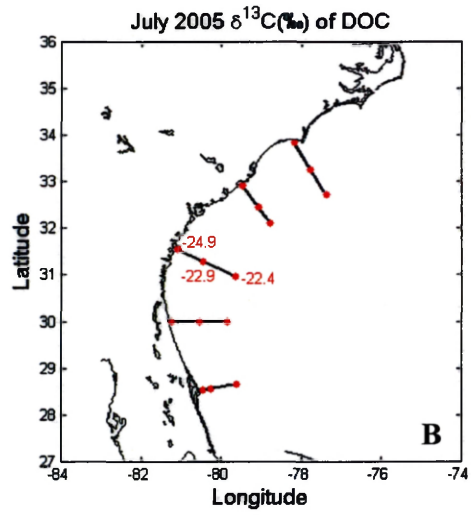
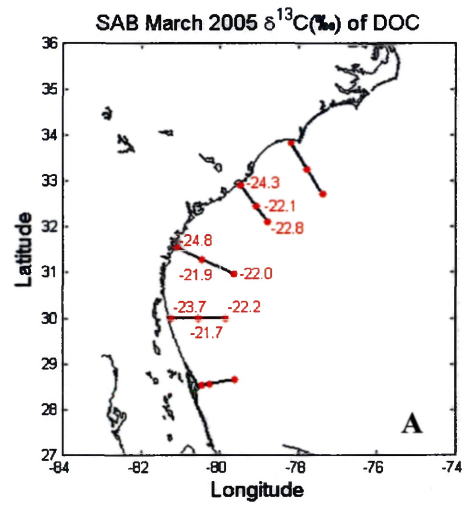


Figure 10. Surface  $\Delta^{14}\text{C}$ -DOC distributions for A) March, B) July, and C) October 2005 cruises to the SAB.

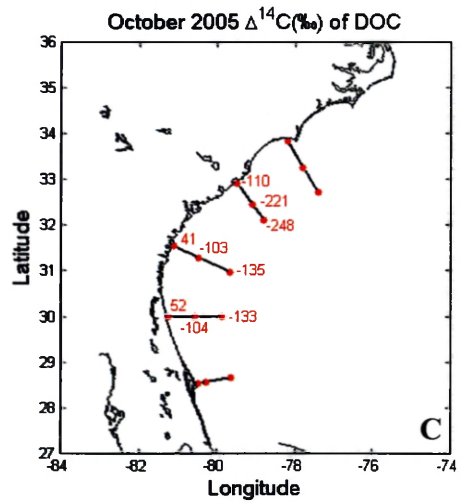
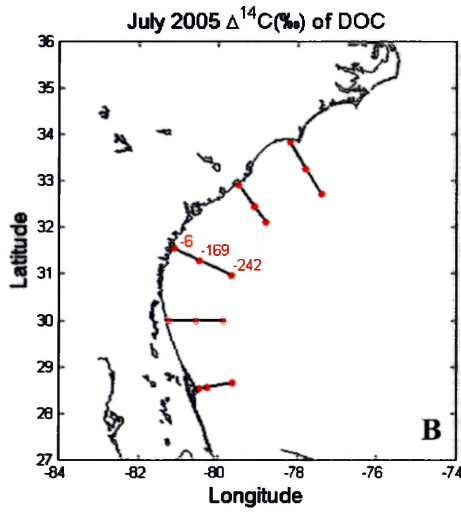
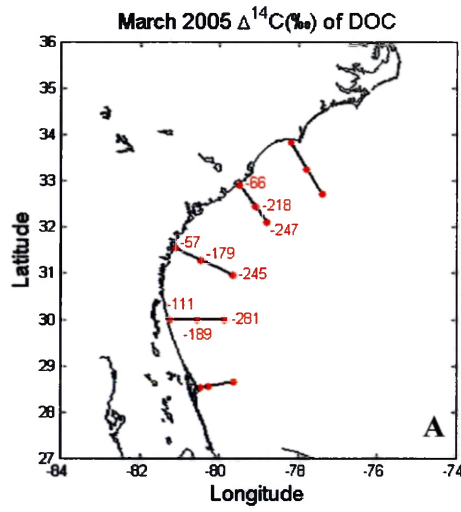


Figure 11. Surface  $\delta^{13}\text{C}$ -POC distributions for A) March, B) July, and C) October 2005 cruises to the SAB.

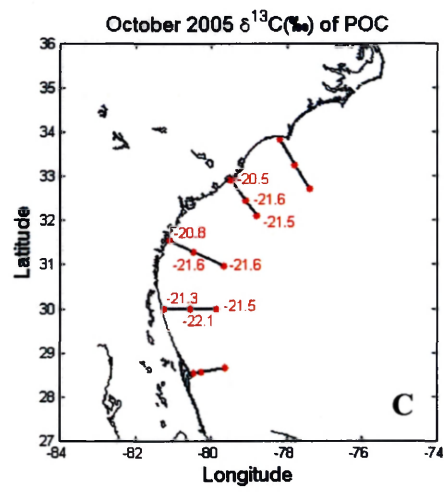
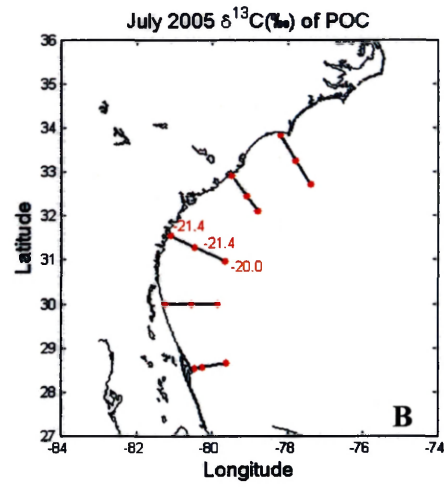
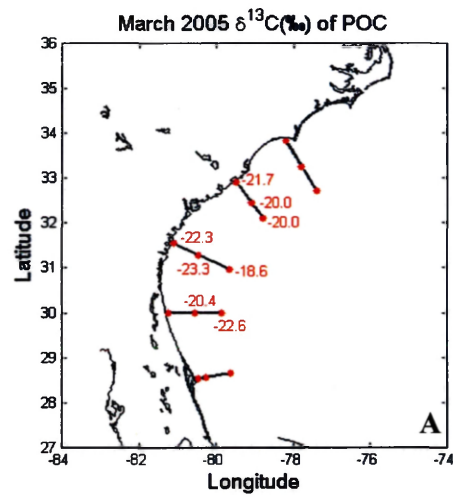




Figure 12. Surface  $\Delta^{14}\text{C}$ -POC distributions for A) March, B) July, and C) October 2005 cruises to the SAB.

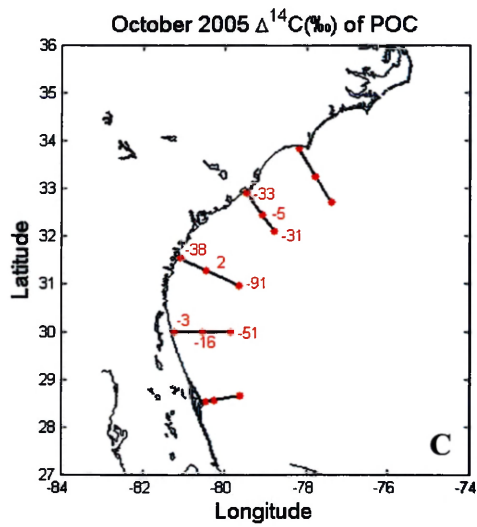
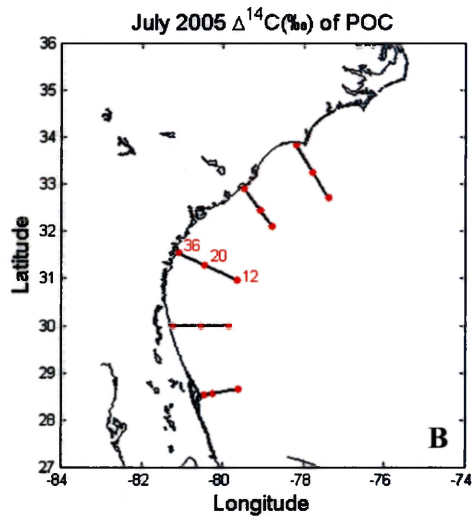
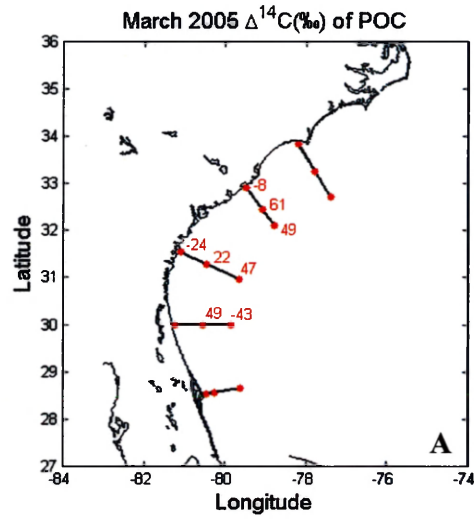


Figure 13. Surface DON distributions for A) March, B) July, and C) October 2005 cruises to the SAB.

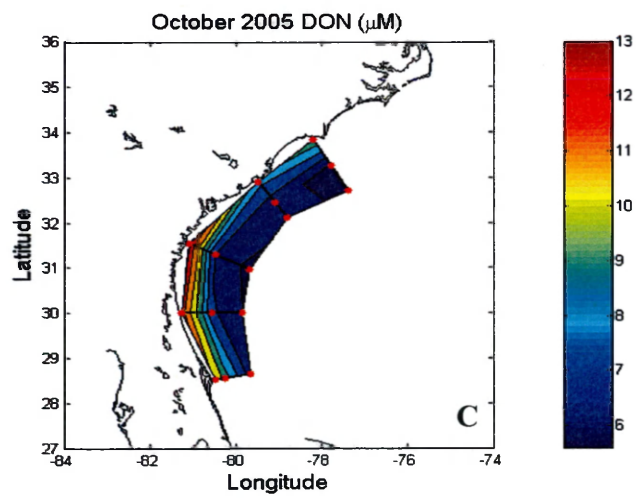
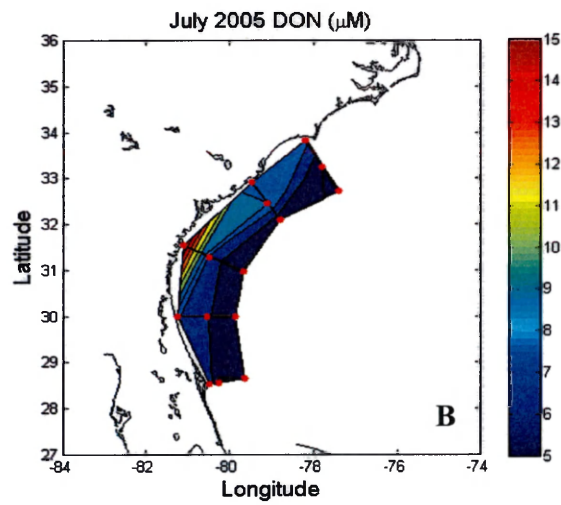
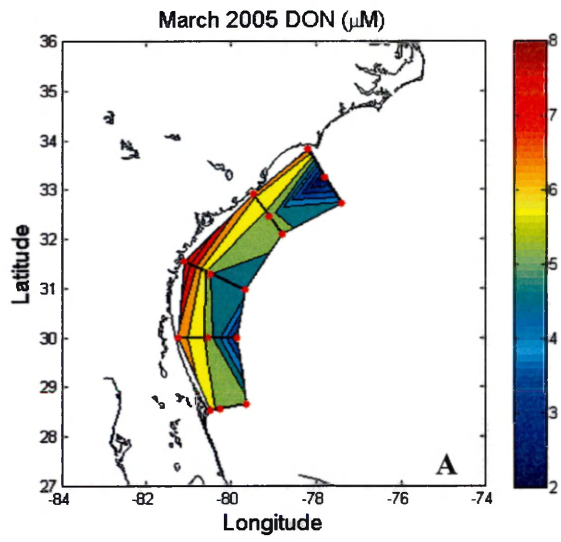


Figure 14. DON depth profiles for A) March, B) July, and C) October 2005 cruises to the SAB. Error bars represent the propagated errors of duplicate sample analyses.

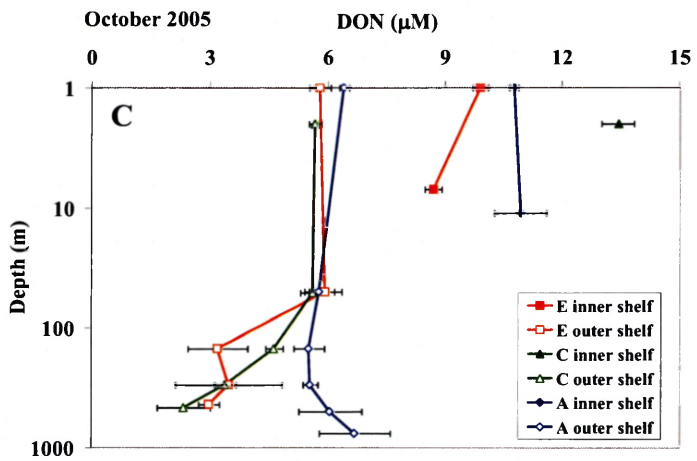
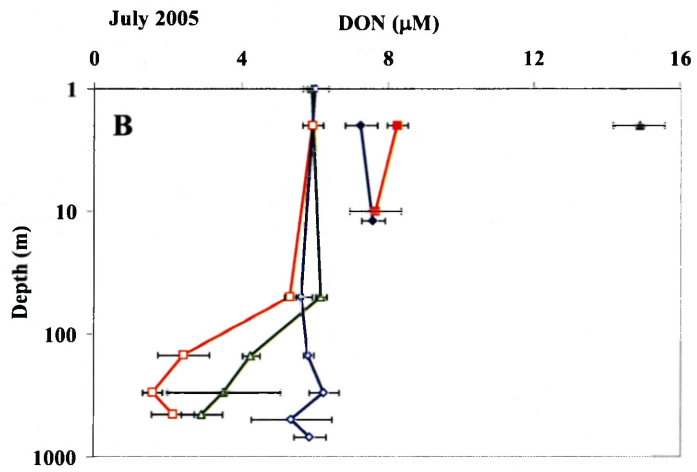
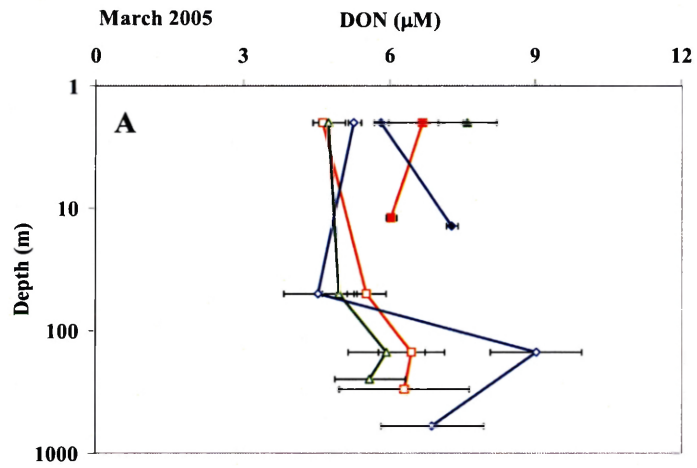


Figure 15. Surface DOP distributions for A) March, B) July, and C) October 2005 cruises to the SAB.

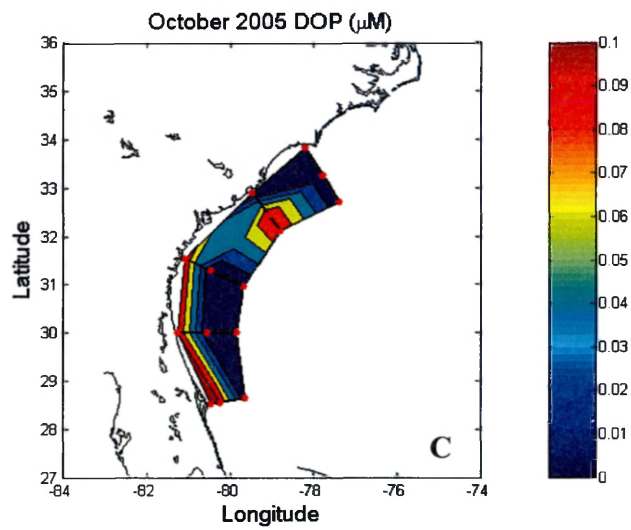
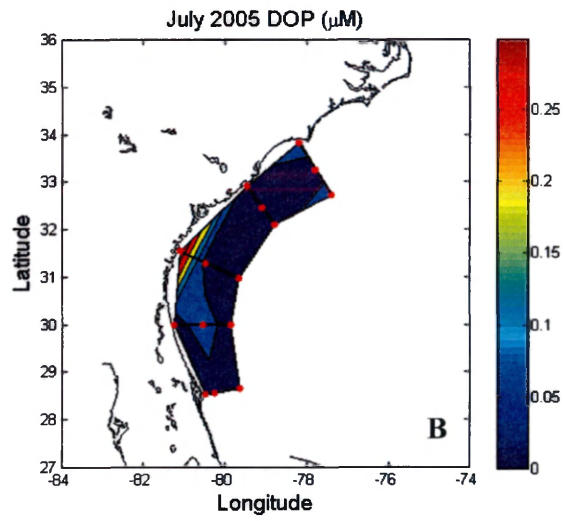
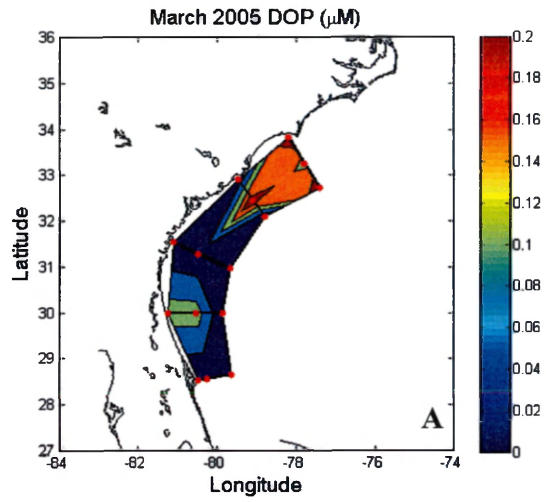




Figure 16. DOP depth profiles for A) March, B) July, and C) October 2005 cruises to the SAB. Error bars represent the propagated errors of duplicate sample analyses.

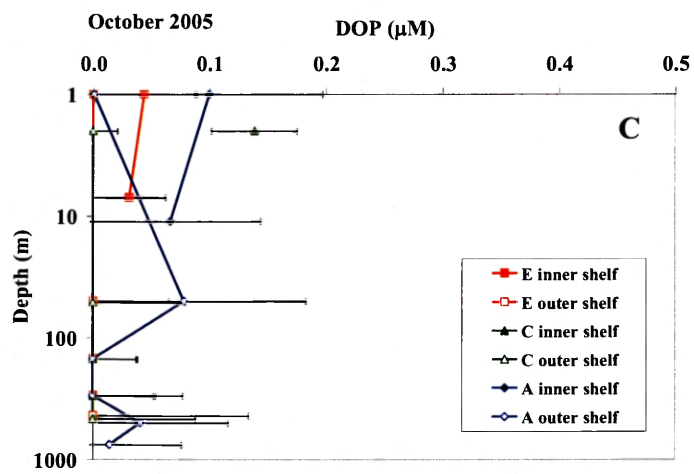
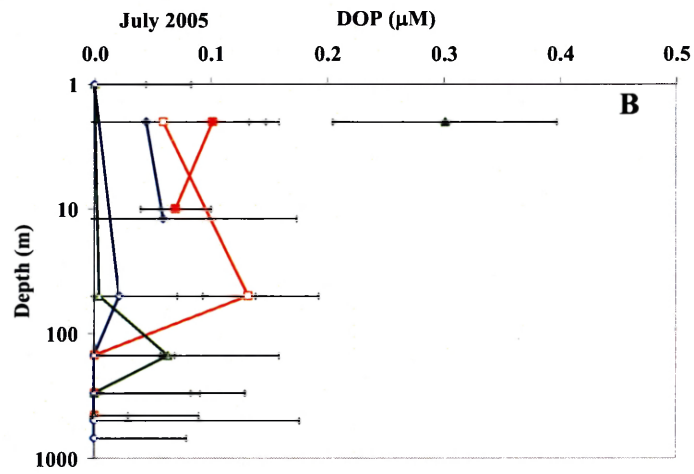
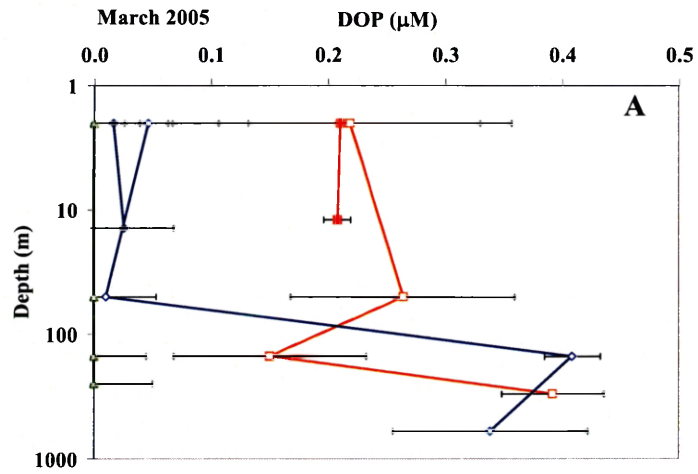


Figure 17. Surface DIC distributions for A) March, B) July, and C) October 2005 cruises to the SAB.

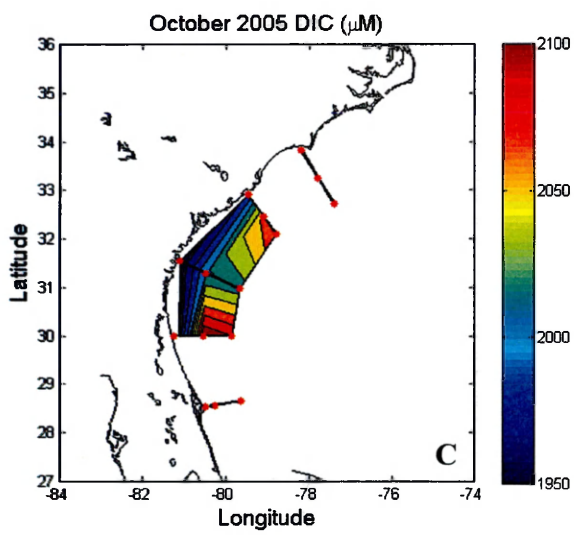
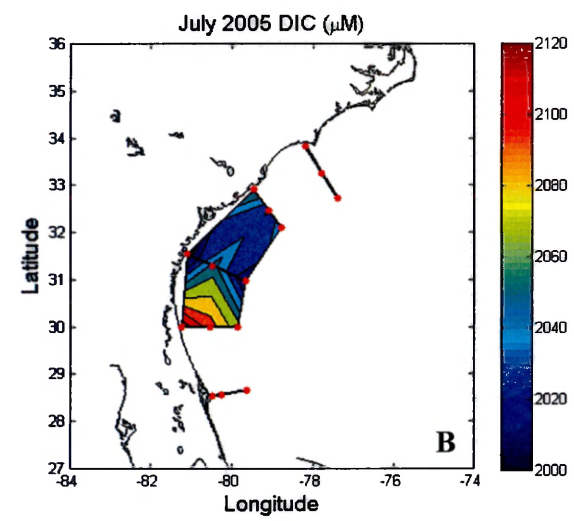
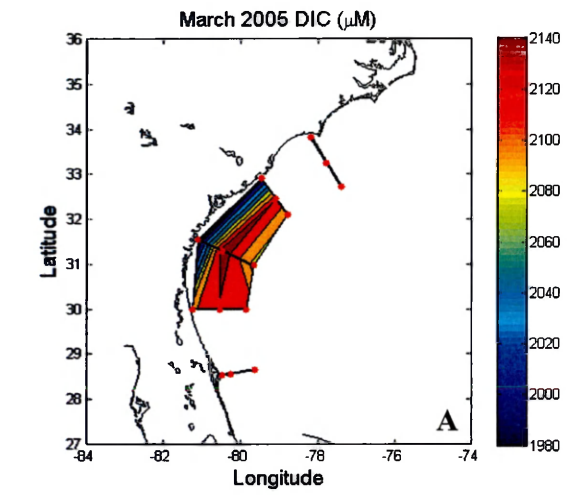


Figure 18. DIC depth profiles for A) March, B) July, and C) October 2005 cruises to the SAB.

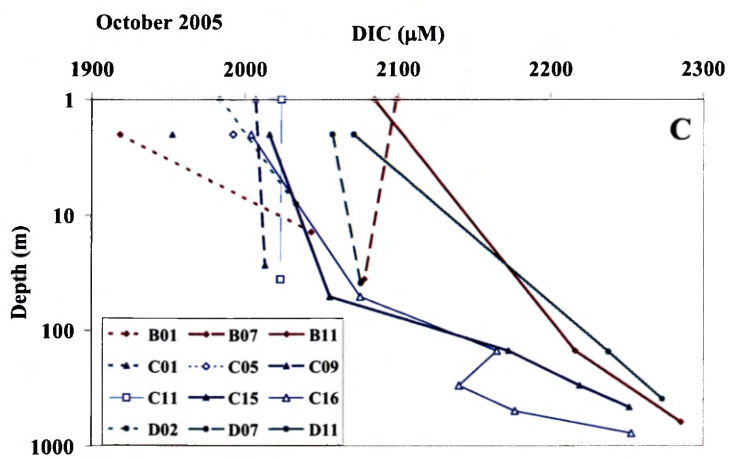
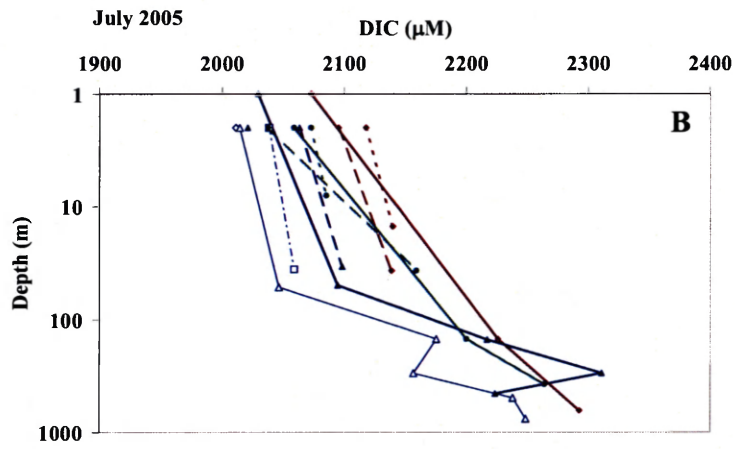
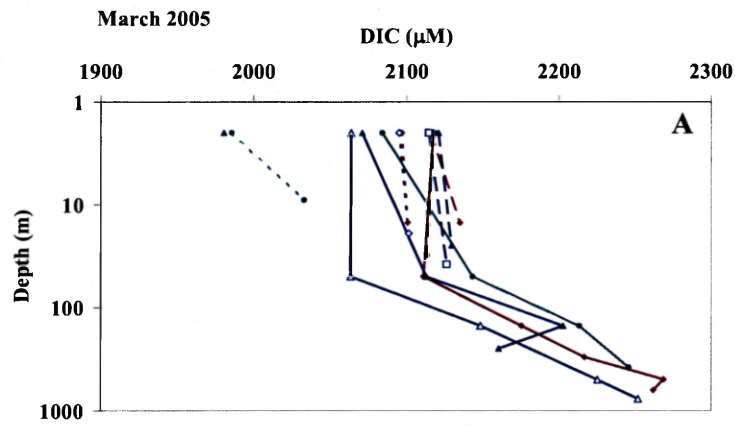


Figure 19. Surface  $\delta^{13}\text{C}$ -DIC distributions for A) March, B) July, and C) October 2005 cruises to the SAB.

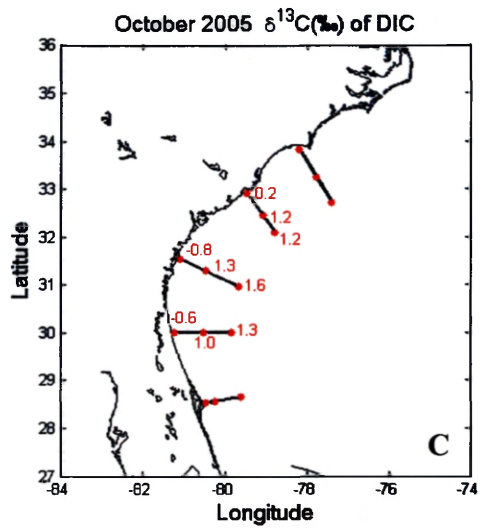
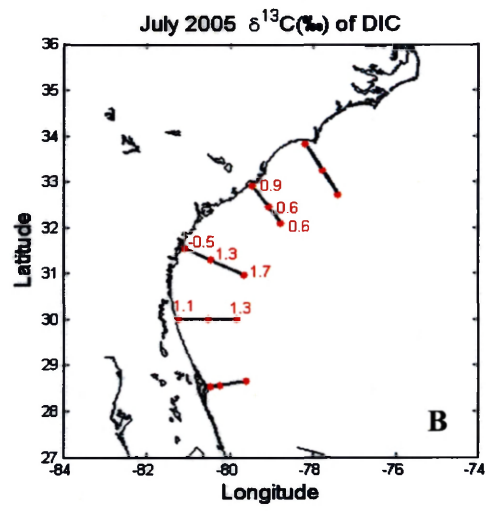
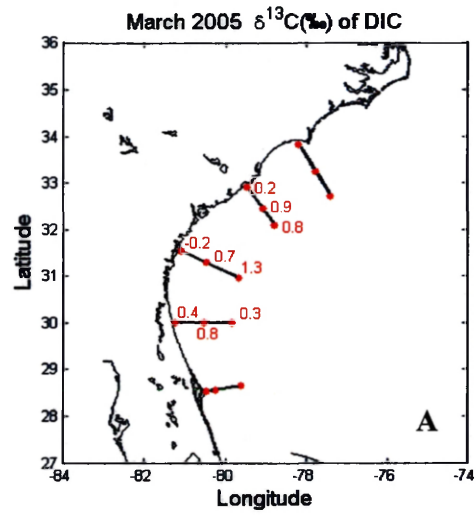




Figure 20.  $\delta^{13}\text{C}$ -DIC depth profiles for A) March, B) July, and C) October 2005 cruises to the SAB.

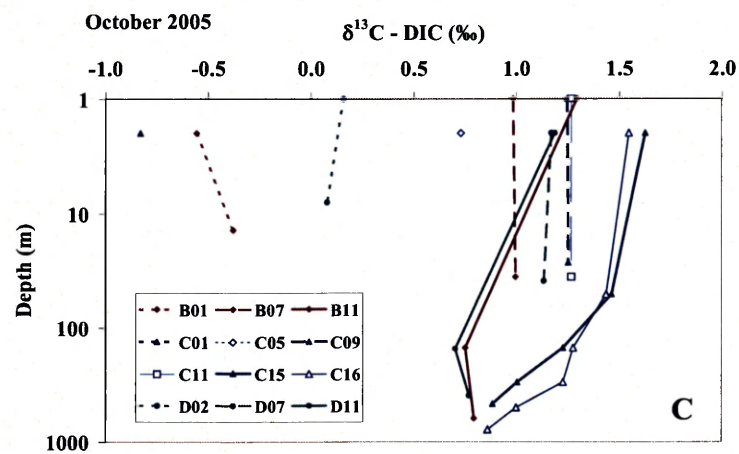
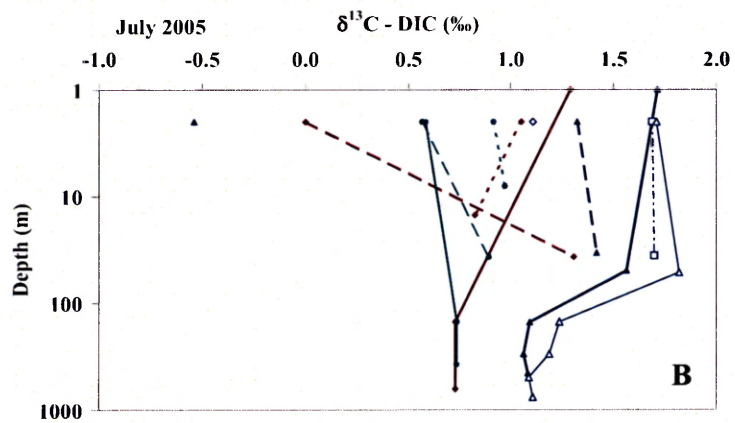
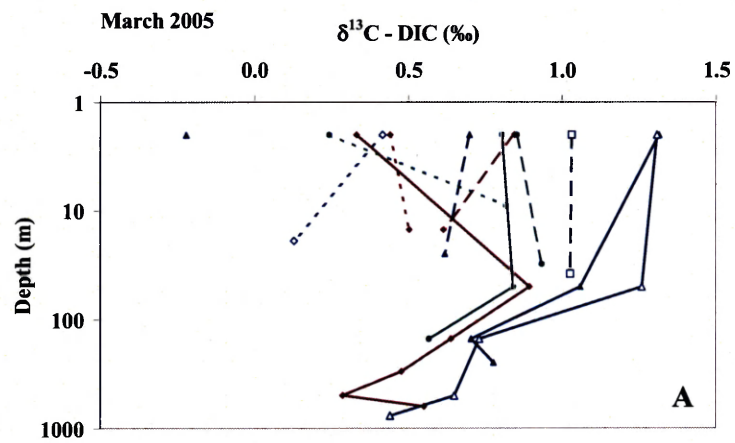


Figure 21. Surface  $\Delta^{14}\text{C}$ -DIC distributions for A) March, B) July, and C) October 2005 cruises to the SAB.

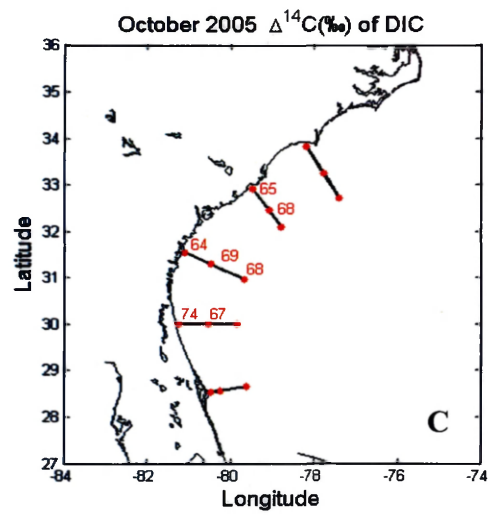
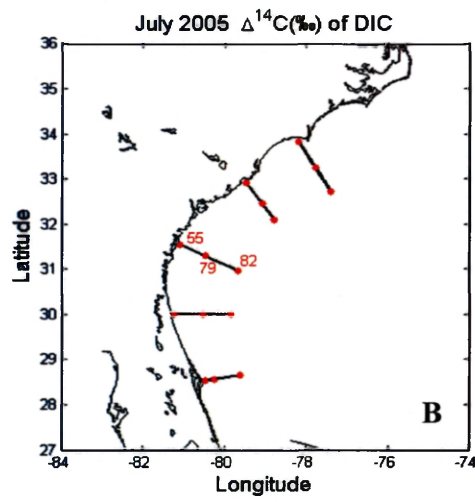
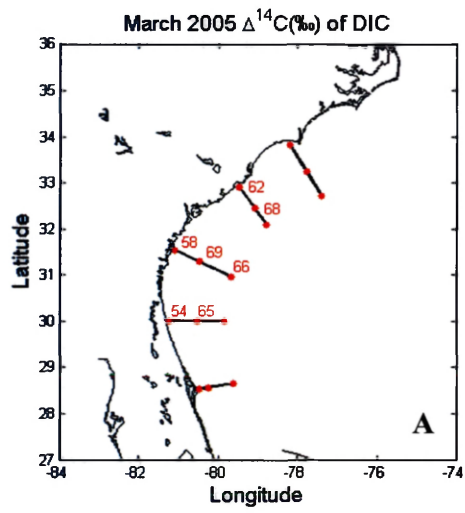


Figure 22.  $\Delta^{14}\text{C}$ -DIC depth profiles for A) March, B) July, and C) October 2005 cruises to the SAB.

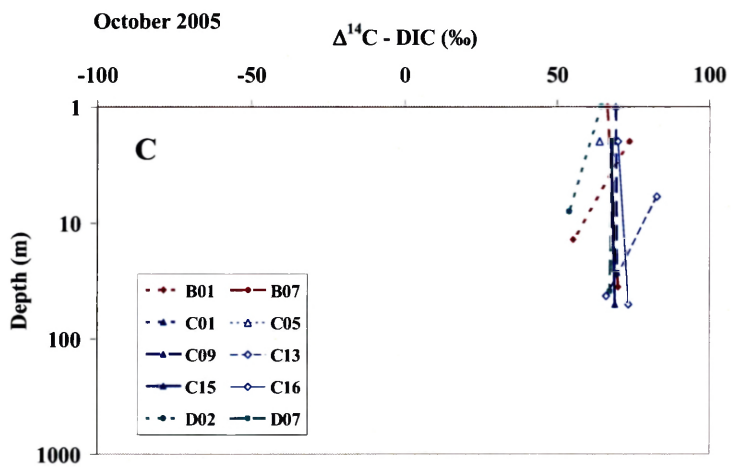
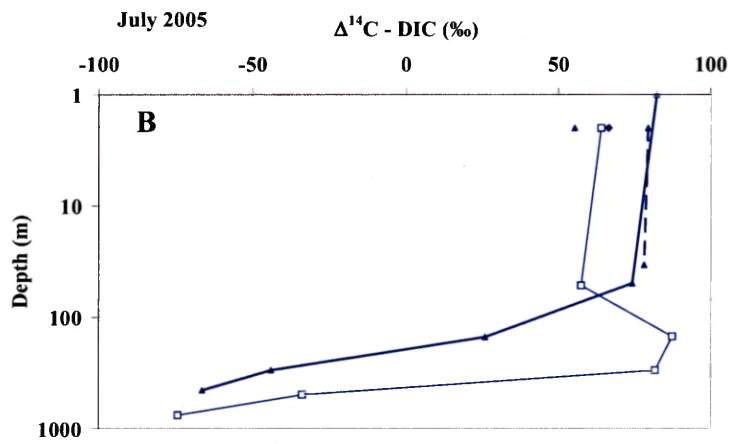
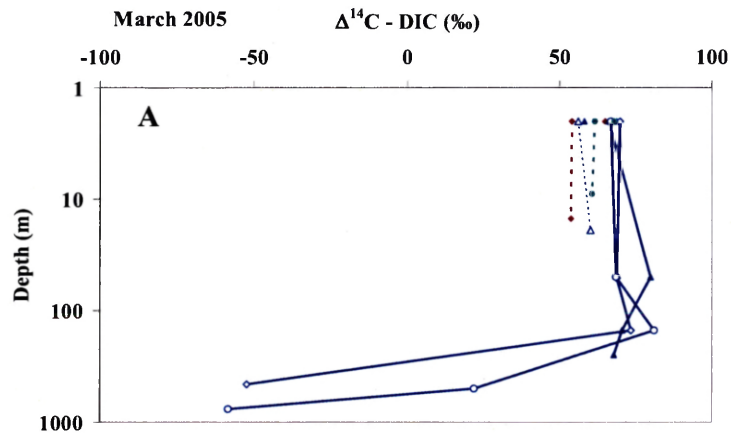
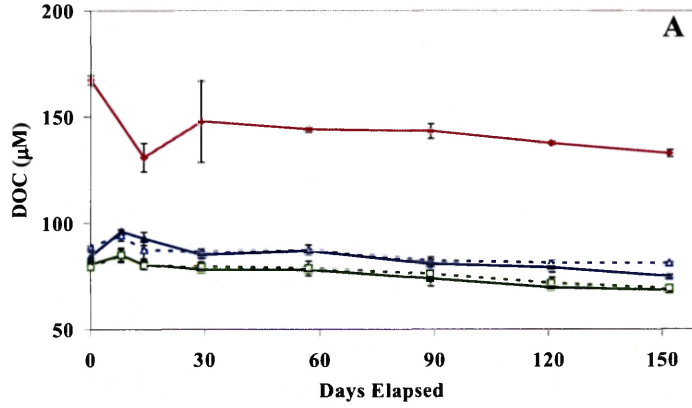


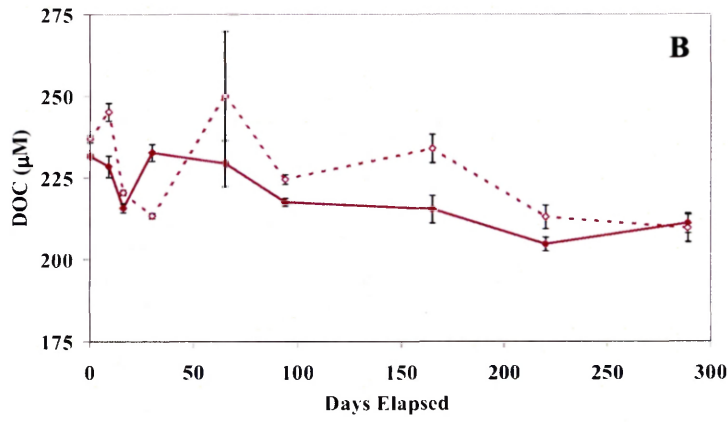
Figure 23. DOM dark decomposition experiment time series changes in DOC concentrations for A) March, B) July, and C) October 2005 cruises to the SAB. “A” and “B” in treatment categories on X axis refer to duplicate 20-L polycarbonate carboy incubations. Error bars represent the standard deviation of triplicate DOC analyses.



March 2005



July 2005



October 2005

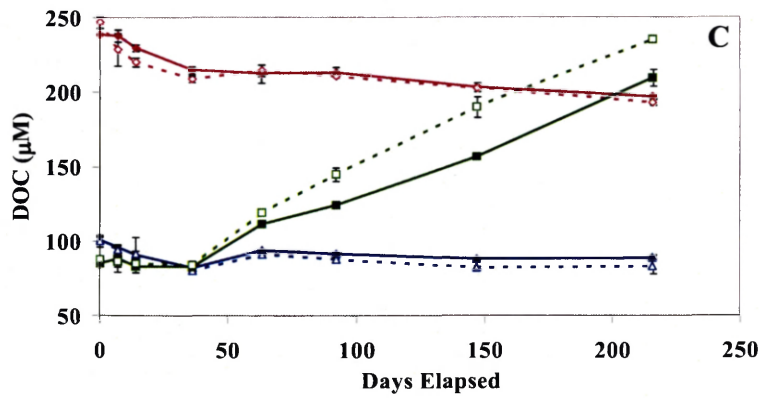
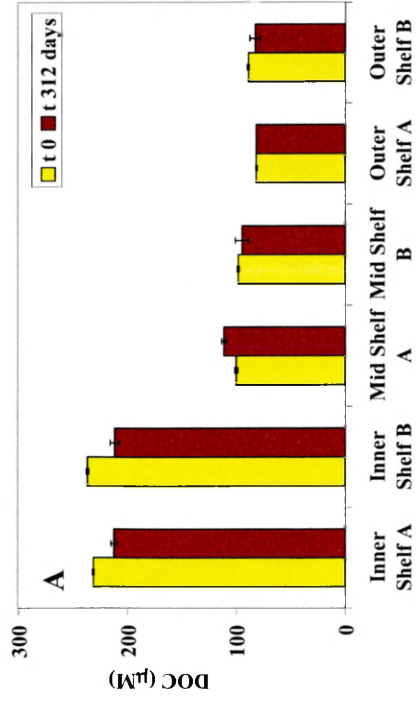


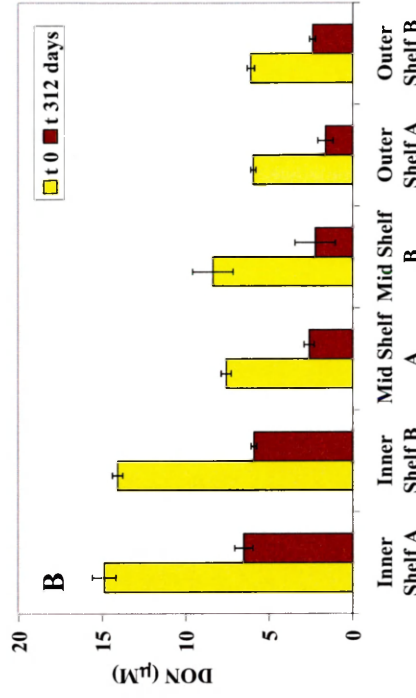


Figure 24. DOM dark decomposition experiment initial and final concentrations for A) July DOC, B) July DON, C) October DOC, and D) October DON. “A” and “B” in treatment categories on X axis refer to duplicate 20-L polycarbonate carboy incubations. Error bars on DOC plots indicate the standard deviation of triplicate DOC analyses. For DON plots, error bars represent propagated errors of duplicate sample analyses.

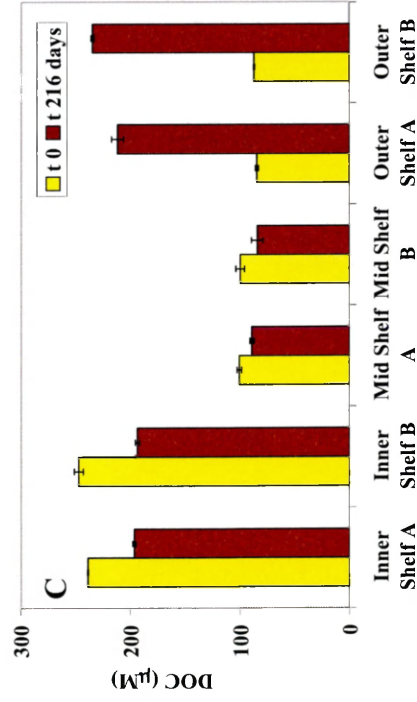
July 2005



July 2005



October 2005



October 2005

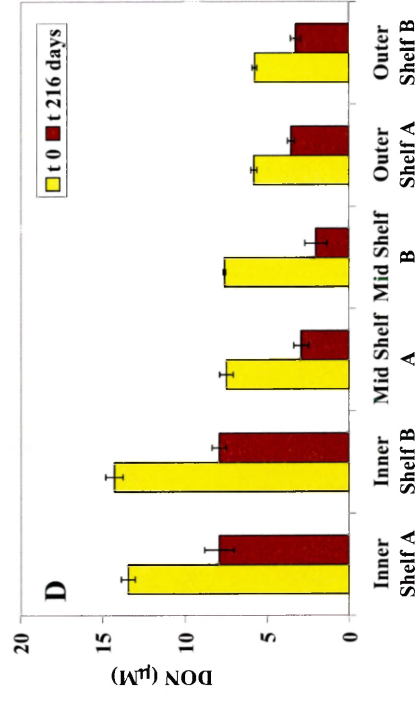
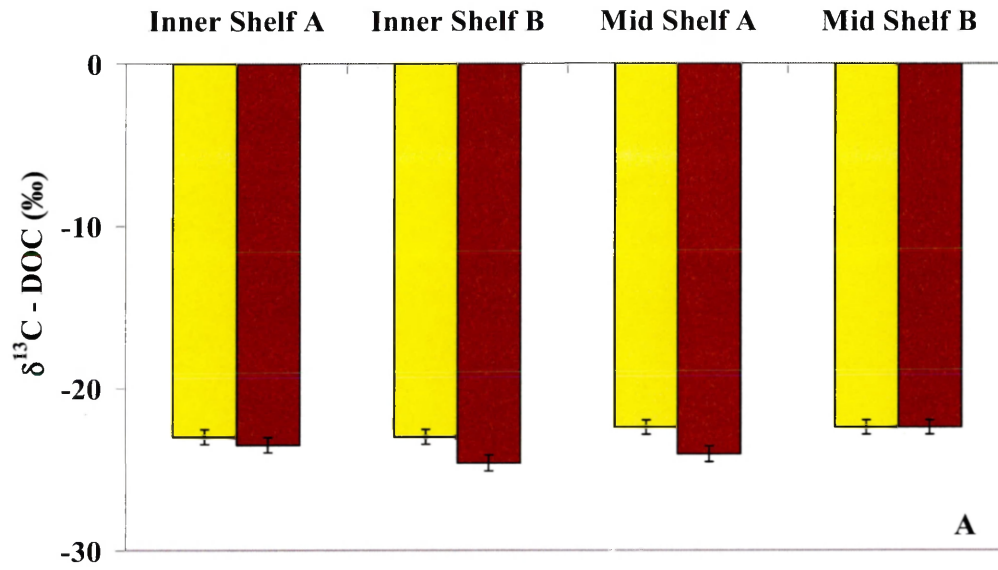


Figure 25. DOM dark decomposition experiment results for A)  $\delta^{13}\text{C}$ -DOC, and B)  $\Delta^{14}\text{C}$ -DOC at  $t=0$  and the conclusion of incubations in October 2005. "A" and "B" in treatment categories on X axis refer to duplicate 20-L polycarbonate carboy incubations. Error bars represent analytical errors.

October 2005



October 2005

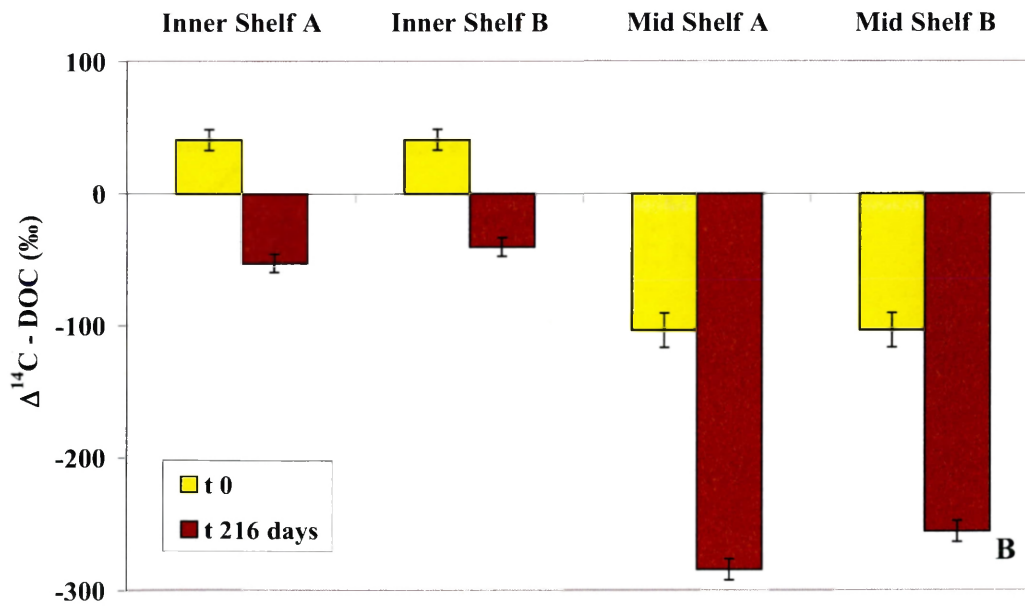


Figure 26. Relationships between A) DOC:DON, B) DOC:DOP, and C) DON:DOP for all samples collected during March, July, and October 2005 cruises to the SAB. Dashed lines represent Redfield stoichiometry.

- ◆ March Inner Shelf    ◇ March Mid Shelf    × March Outer Shelf
- July Inner Shelf    ◇ July Mid Shelf    × July Outer Shelf
- October Inner Shelf    ◇ October Mid Shelf    × October Outer Shelf

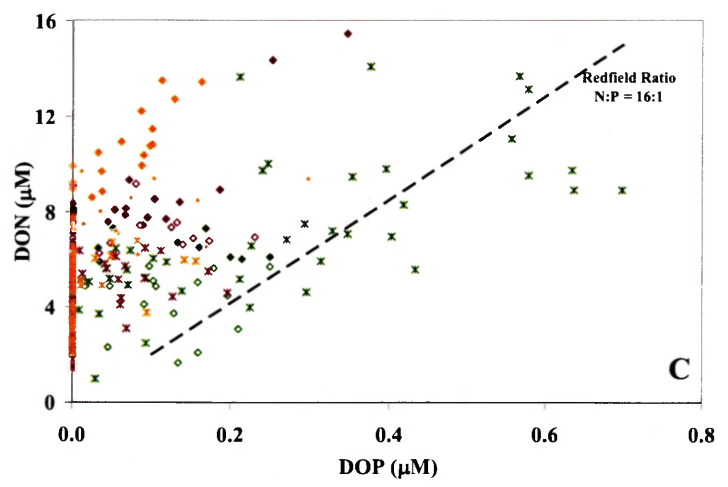
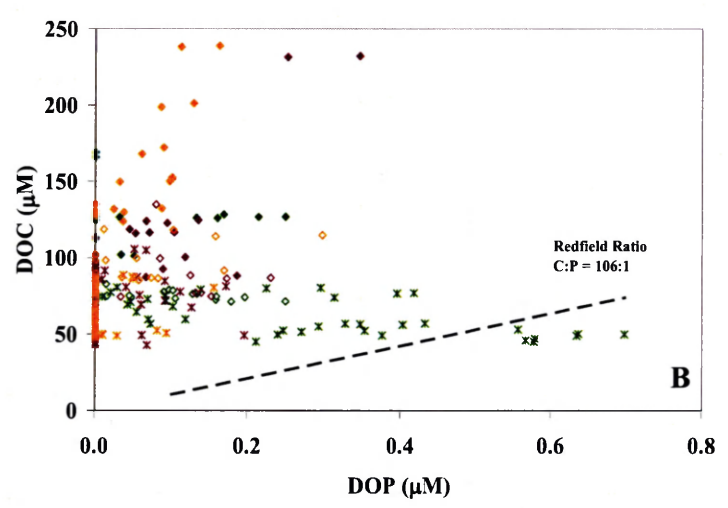
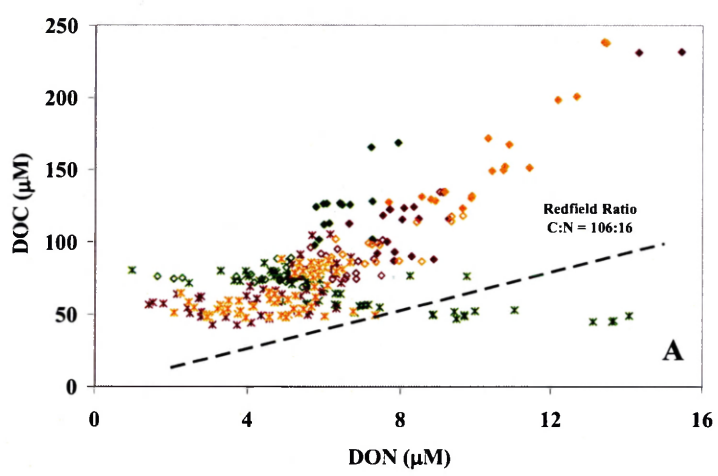


Figure 27. Surface DOC:DON distributions for A) March, B) July, and C) October 2005 cruises to the SAB. Note different scales for each panel.

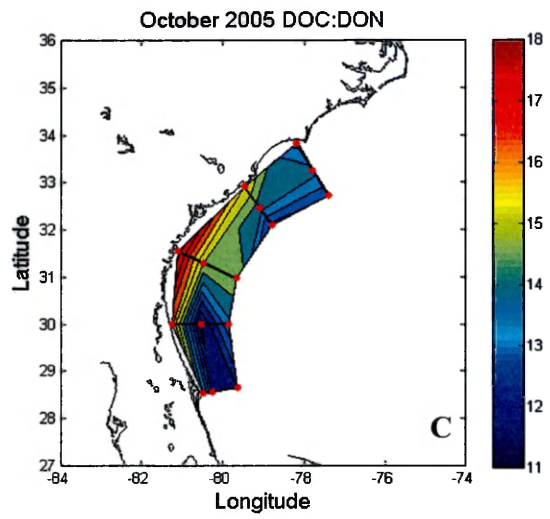
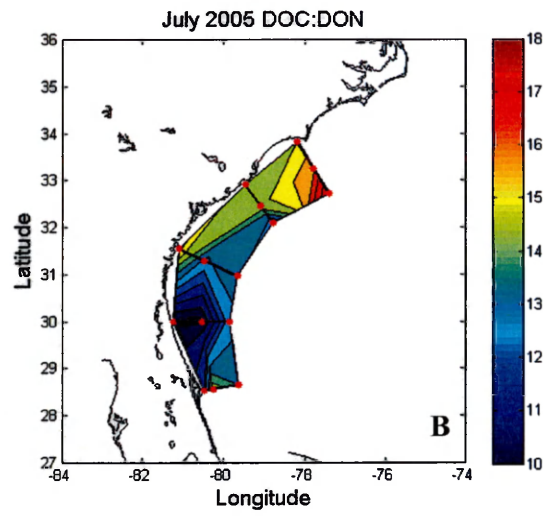
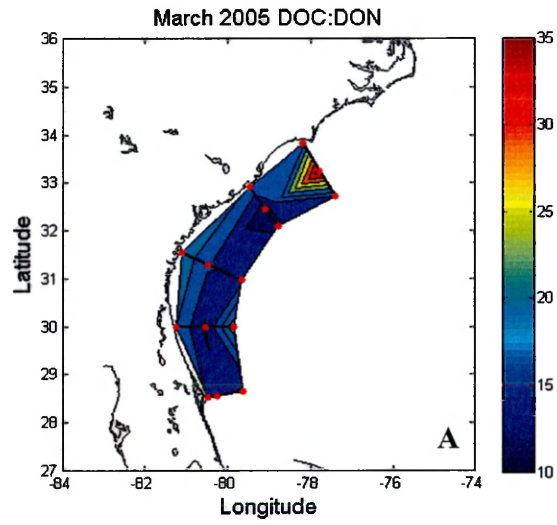




Figure 28. DOC:DON depth profiles for A) March, B) July, and C) October 2005 cruises to the SAB. Error bars represent propagated errors of duplicate sample analyses.

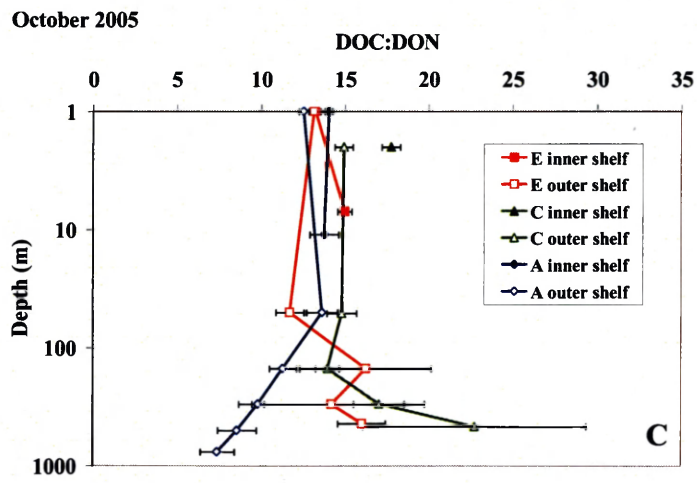
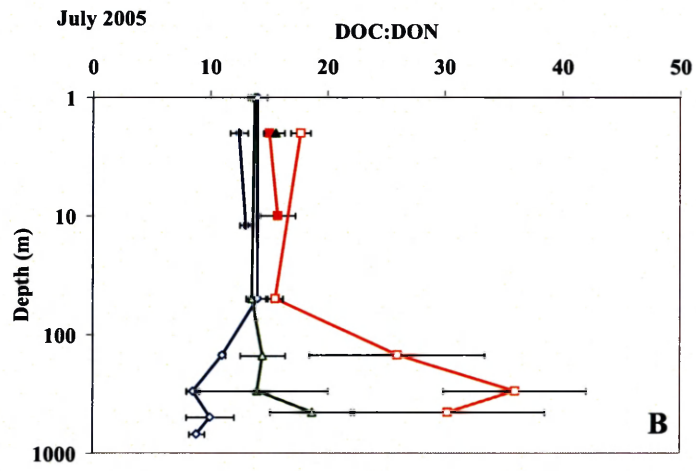
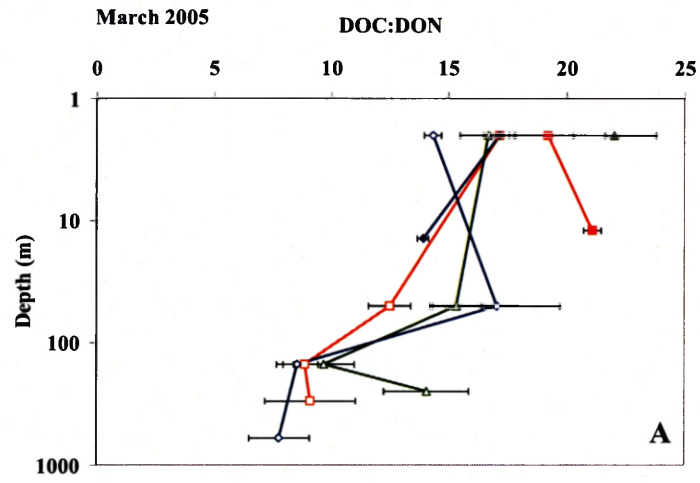


Figure 29. Salinity mixing relationships for A) DOC concentration, B)  $\delta^{13}\text{C}$ -DOC and C)  $\Delta^{14}\text{C}$ -DOC for surface samples only from March, July and October 2005 cruises to the SAB. Solid lines or curves indicate the predicted conservative distributions between the average of August 2006 riverine end members ( $S < 3$ ) and yearly averaged outer shelf surface marine end members (at  $S \approx 36$ ). Red dashed lines represent linear regressions for all surface samples.

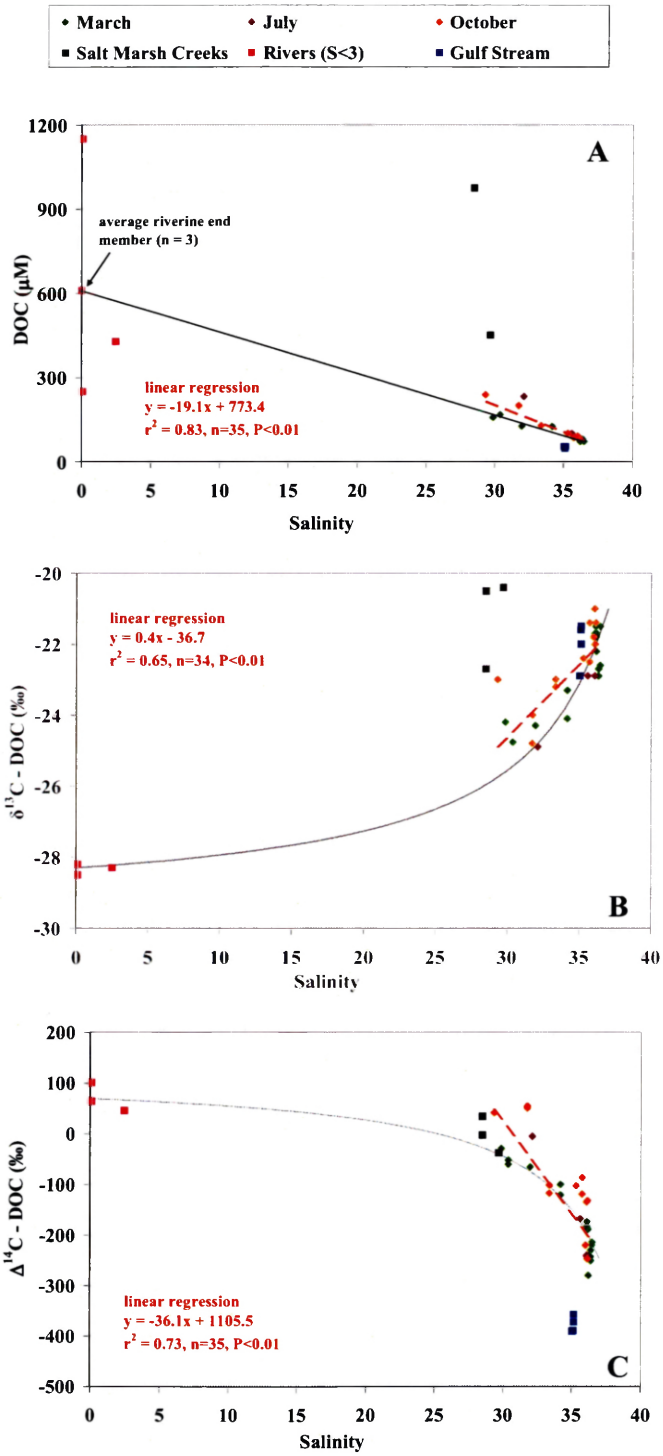


Figure 30. Surface DOC property-property relationships for A)  $\delta^{13}\text{C}$ - DOC vs. DOC concentration and B)  $\Delta^{14}\text{C}$ -DOC vs. DOC concentration for surface samples from March, July and October 2005 cruises to the SAB. Lines represent linear correlations between parameters and colors correspond to the three sampling periods.

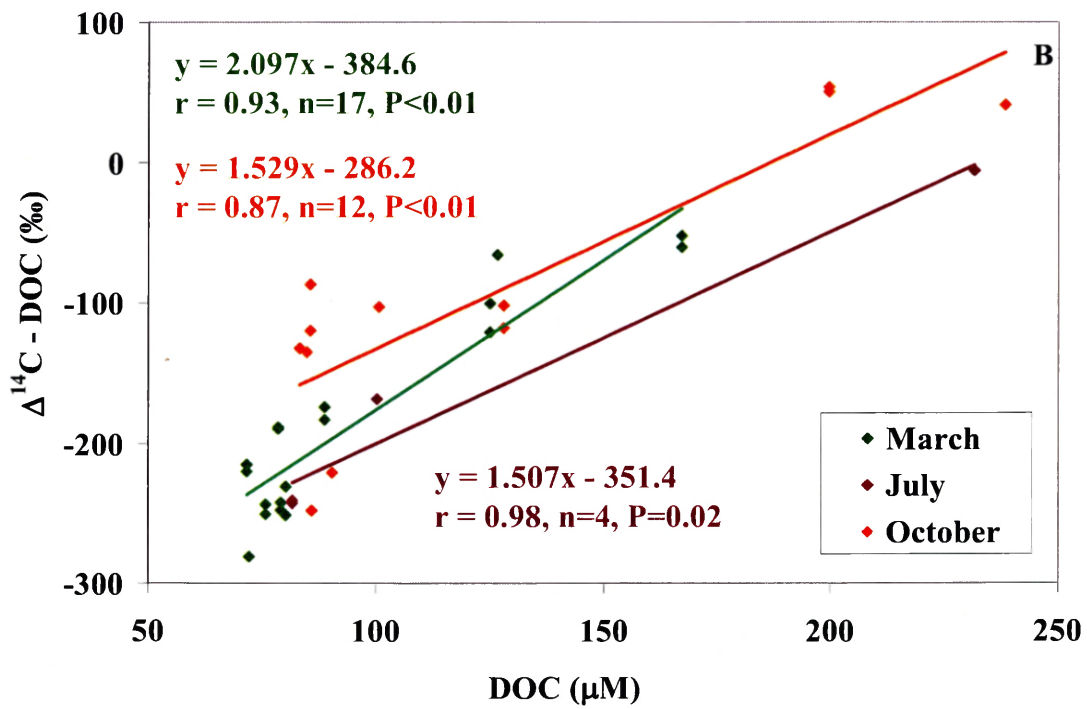
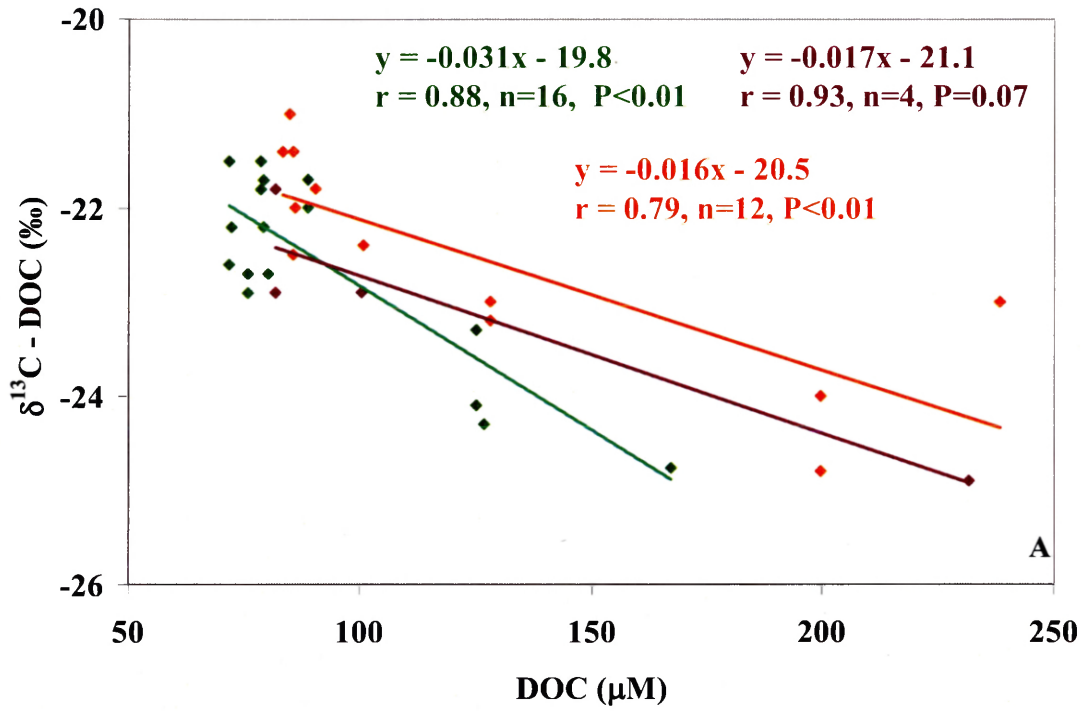


Figure 31. Surface DOC property-property relationships for A) DOC:DON vs.  $\delta^{13}\text{C}$ -DOC and B) DOC:DON vs.  $\Delta^{14}\text{C}$ -DOC for surface samples from March, July and October 2005 cruises to the SAB. Lines represent best-fit linear correlations between parameters and colors correspond to the three sampling periods.

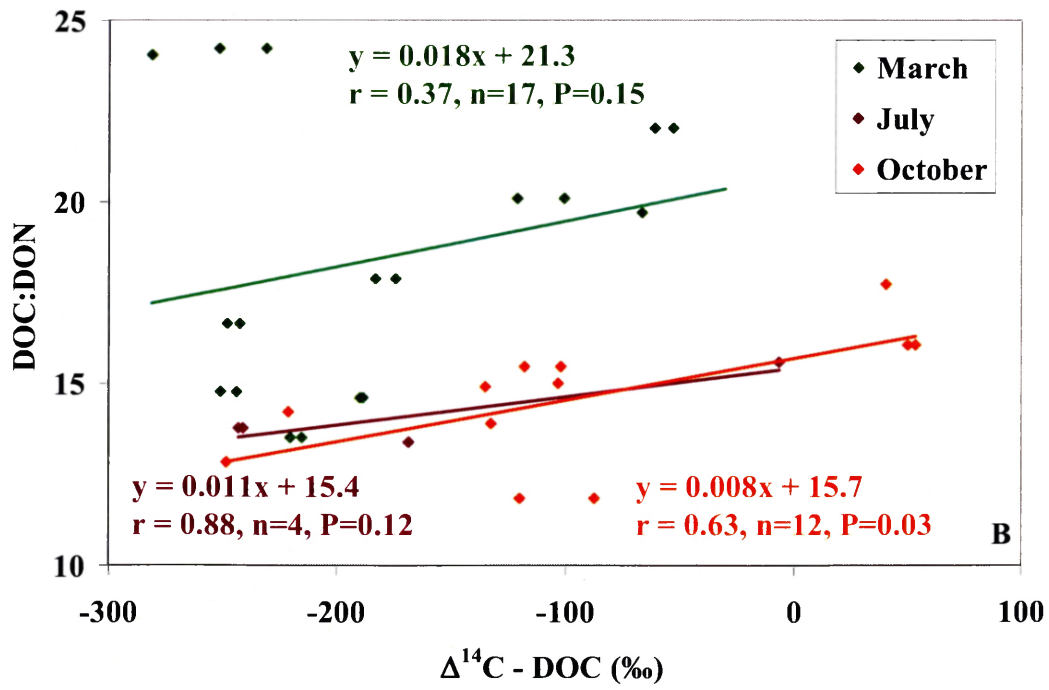
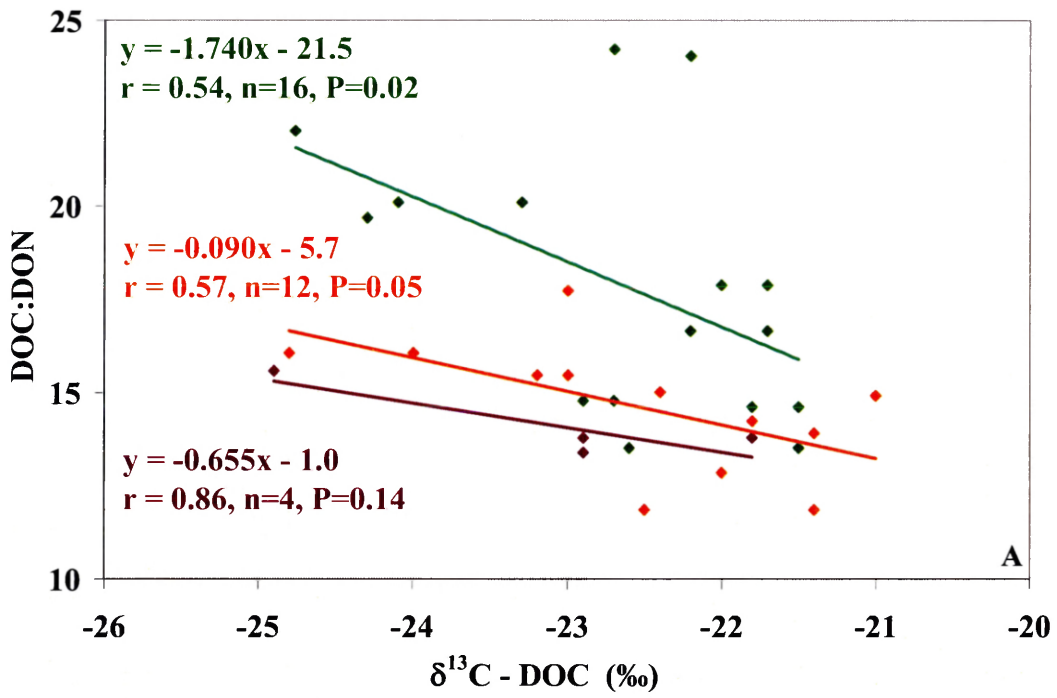




Figure 32.  $\Delta^{14}\text{C}$ -DOC vs.  $\delta^{13}\text{C}$ -DOC from March, July, and October 2005 cruises to the SAB for A) surface samples and B) surface samples and potential end members. Solid line represents best-fit linear correlation for all surface samples.

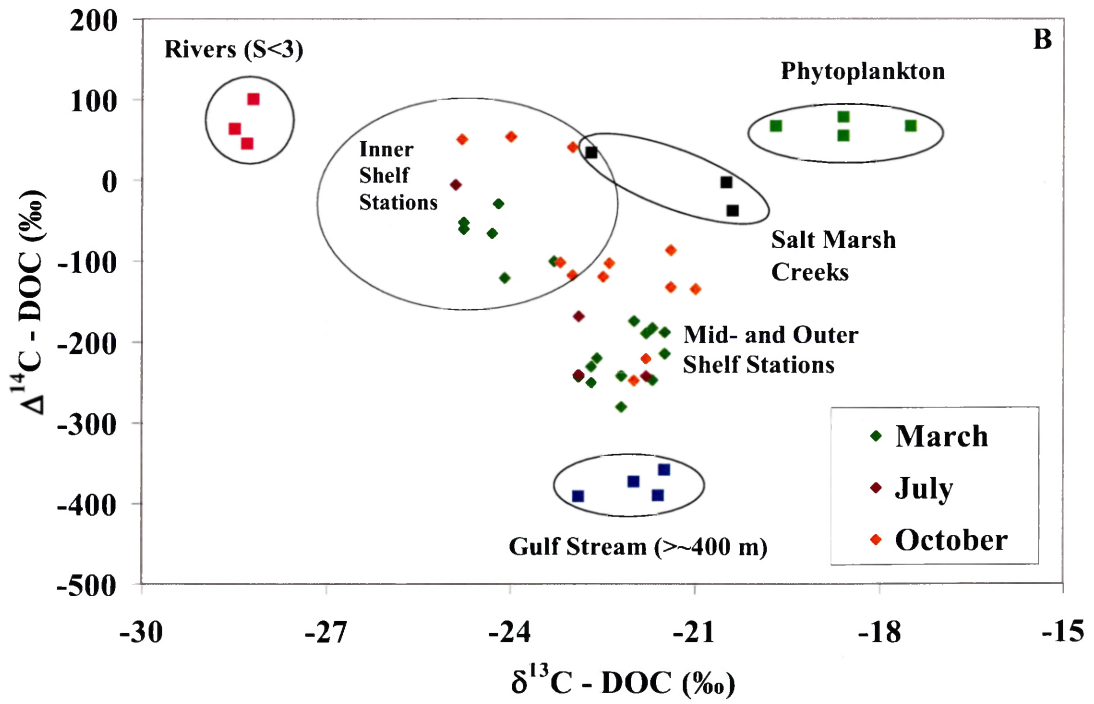
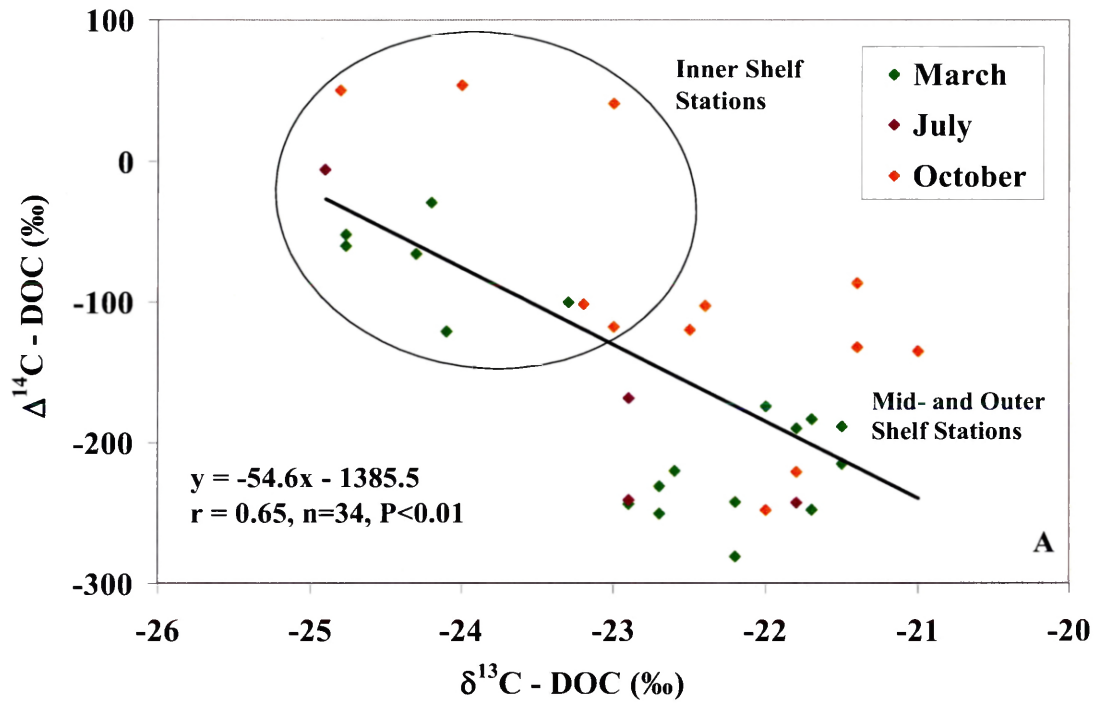


Figure 33. Salinity mixing relationships for A) POC concentration, B)  $\delta^{13}\text{C}$ -POC, and C)  $\Delta^{14}\text{C}$ -POC for surface samples only from March, July and October 2005 cruises to the SAB. Solid lines or curves indicate the predicted conservative distributions between the average of August 2006 riverine end members ( $S < 3$ ) and yearly averaged outer shelf surface marine end members (at  $S \approx 36$ ). Red dashed lines represent linear regressions for all surface samples from March, July and October.

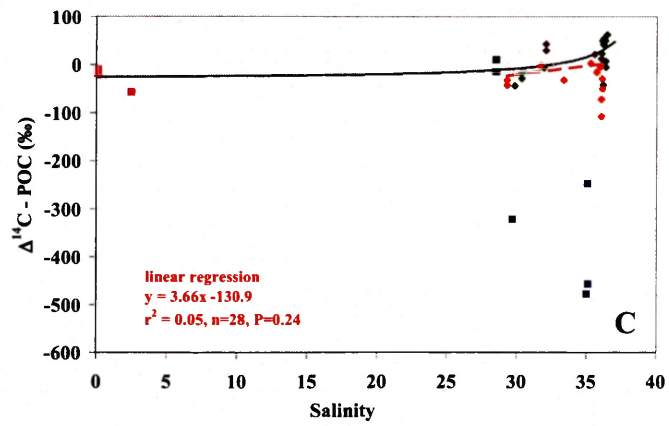
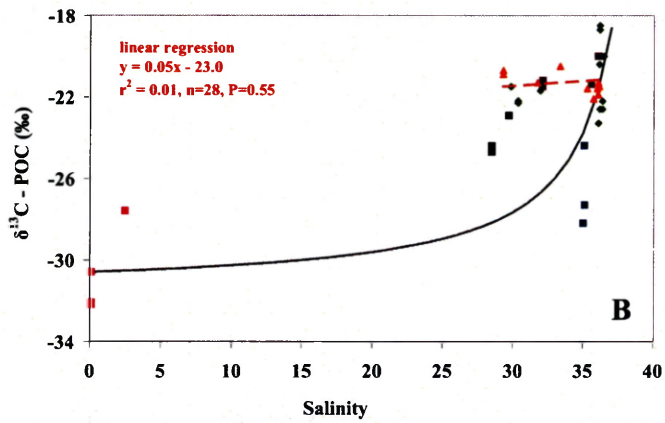
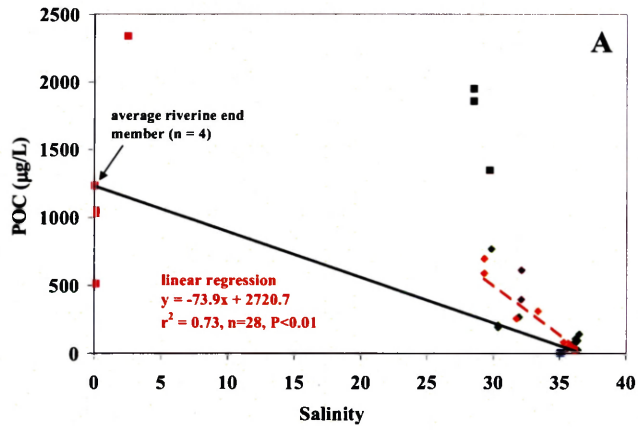
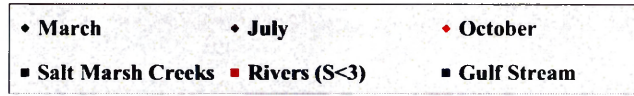


Figure 34.  $\Delta^{14}\text{C}$ -POC vs.  $\delta^{13}\text{C}$ -POC from March, July, and October 2005 cruises to the SAB for A) surface samples and B) surface samples and potential end members. Solid line represents best-fit linear correlation for all surface samples.

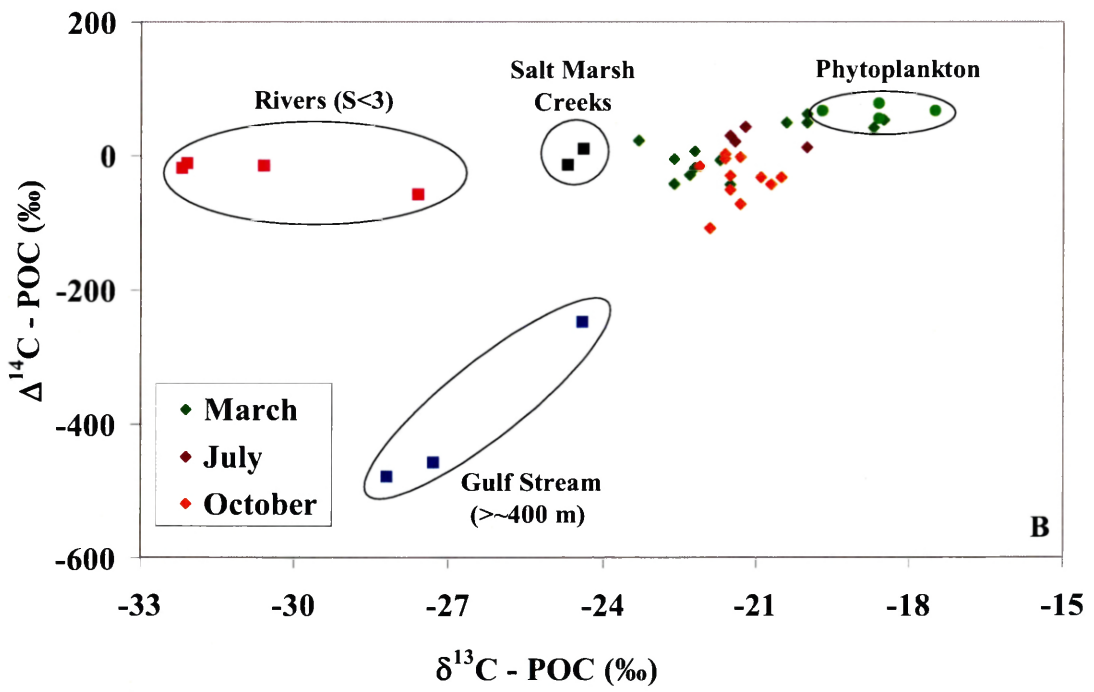
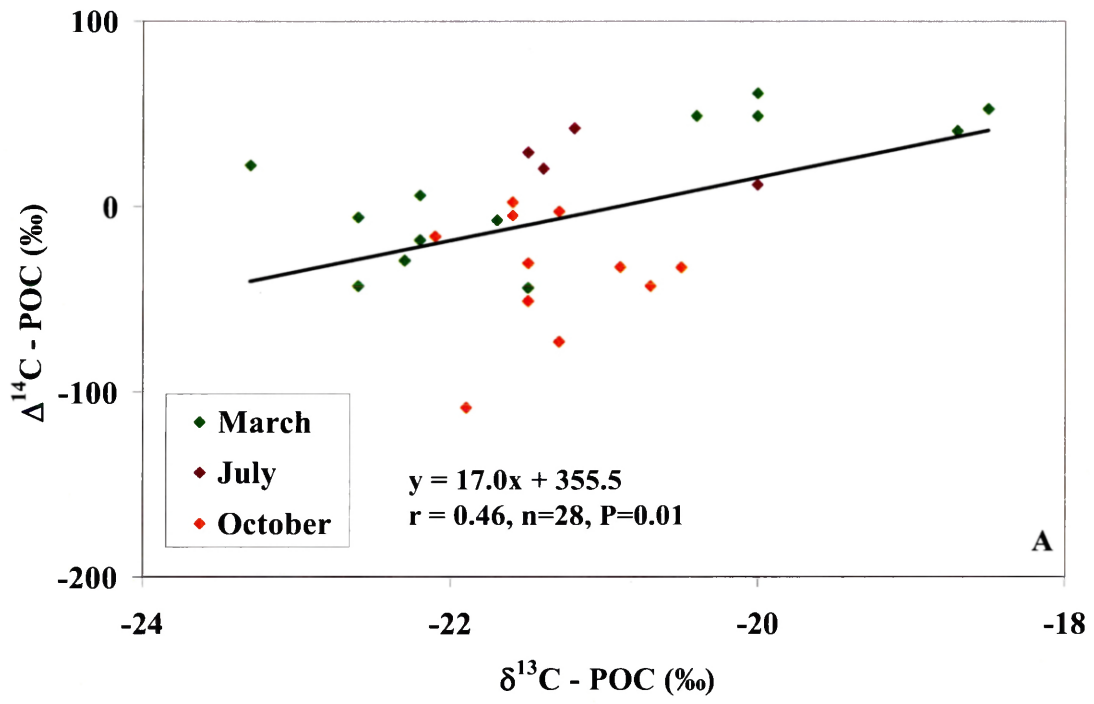


Figure 35. Salinity mixing relationships for A) DIC concentration, B)  $\delta^{13}\text{C}$ -DIC, and C)  $\Delta^{14}\text{C}$ - for surface and deep samples from March, July and October 2005 cruises to the SAB. Lines or curves represent conservative distributions between the average of August 2006 freshwater end members (at  $S=0$ ) and yearly averaged outer shelf marine end members (at  $S\sim 36$ ). Red dashed lines represent linear regressions for all surface samples from March, July and October.

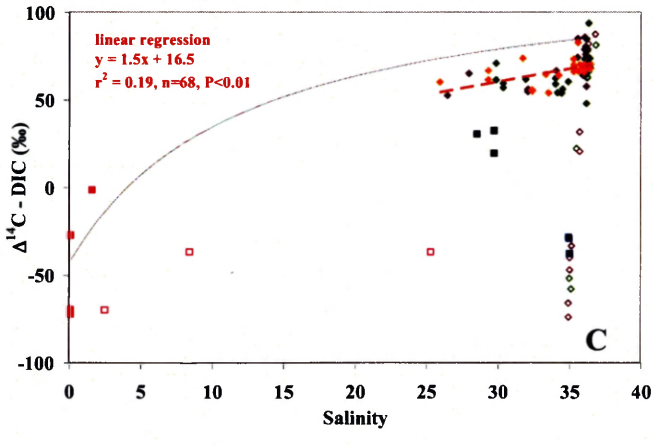
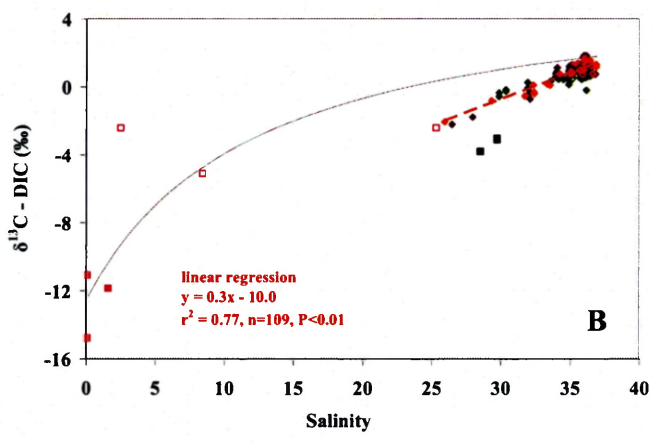
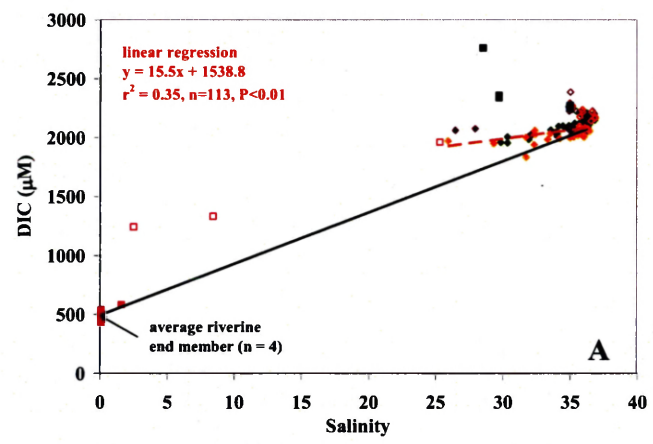
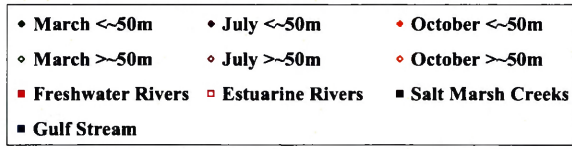




Figure 36.  $\Delta^{14}\text{C-DIC}$  vs.  $\delta^{13}\text{C-DIC}$  from March, July, and October 2005 cruises to the SAB for A) surface and deep samples and B) surface and deep samples plus potential end members. Solid line represents best-fit linear correlation for all surface samples.

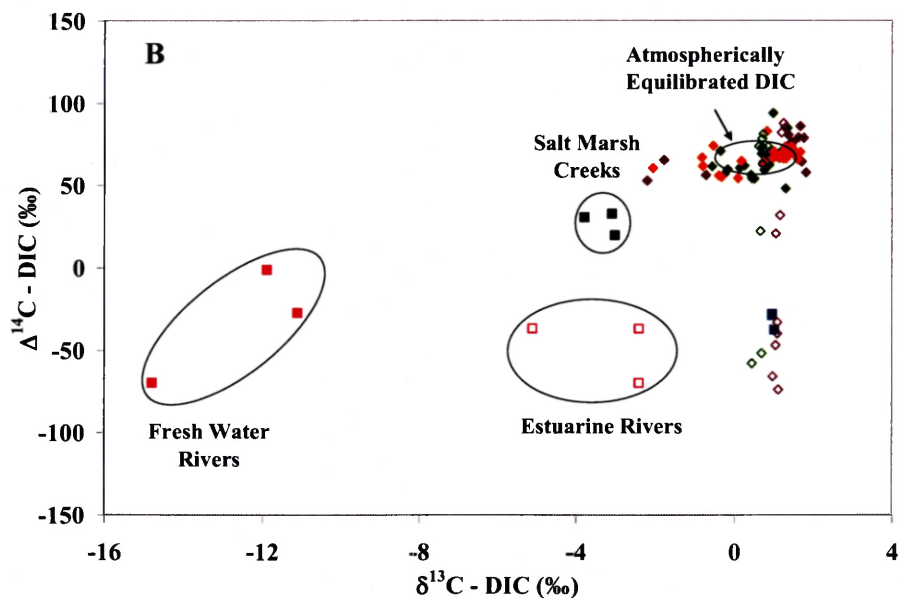
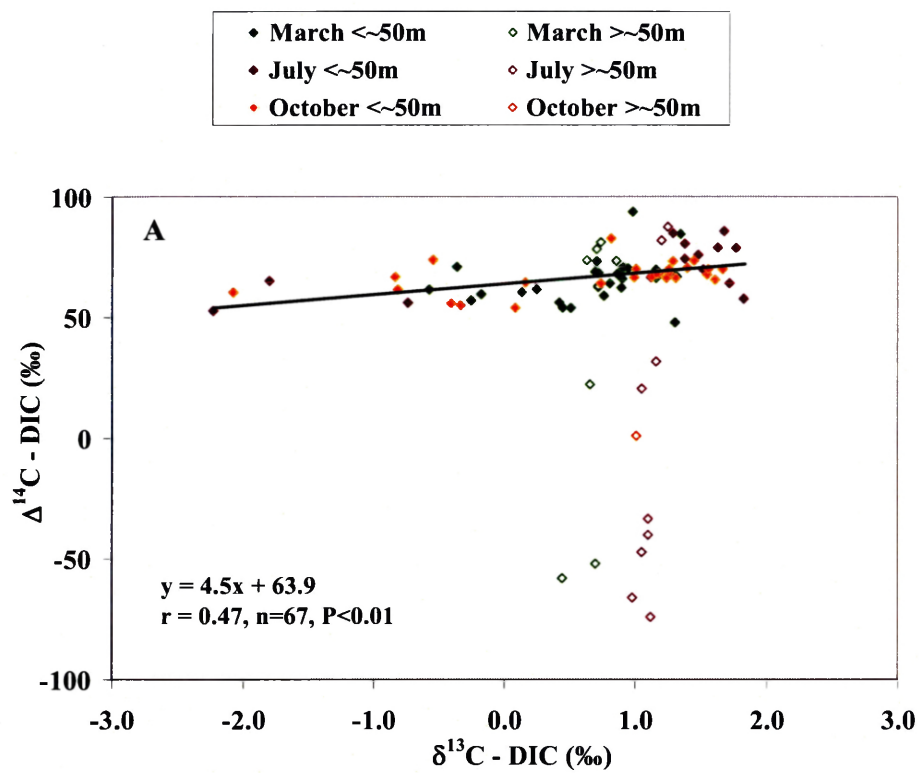
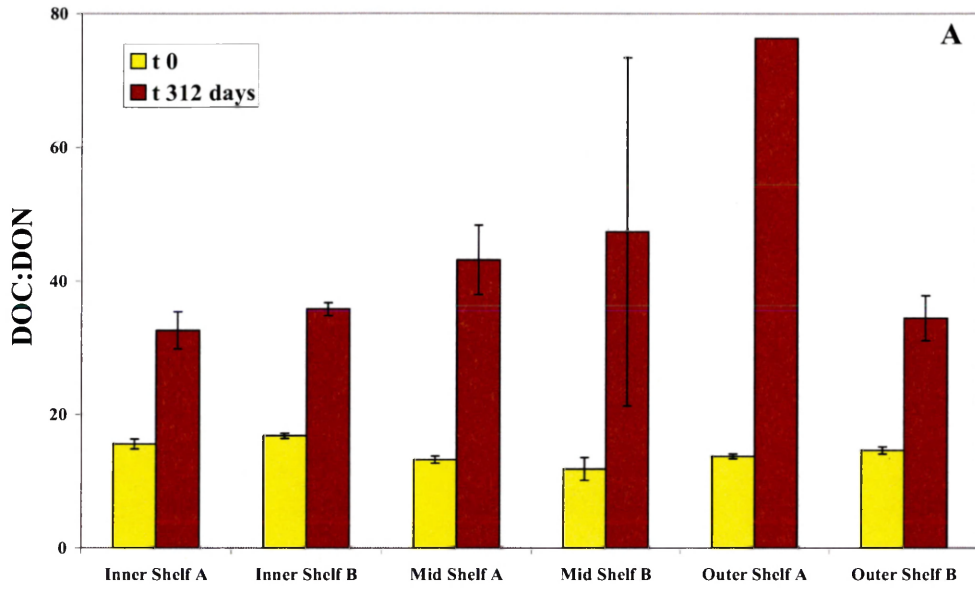


Figure 37. DOC:DON stoichiometry for DOM dark decomposition experiments in A) July and B) October 2005 at t=0 and conclusion of incubations. "A" and "B" in treatment categories on X axis refer to duplicate 20-L polycarbonate carboy incubations. Error bars represent propagated error of duplicate sample analyses.

### July 2005



### October 2005

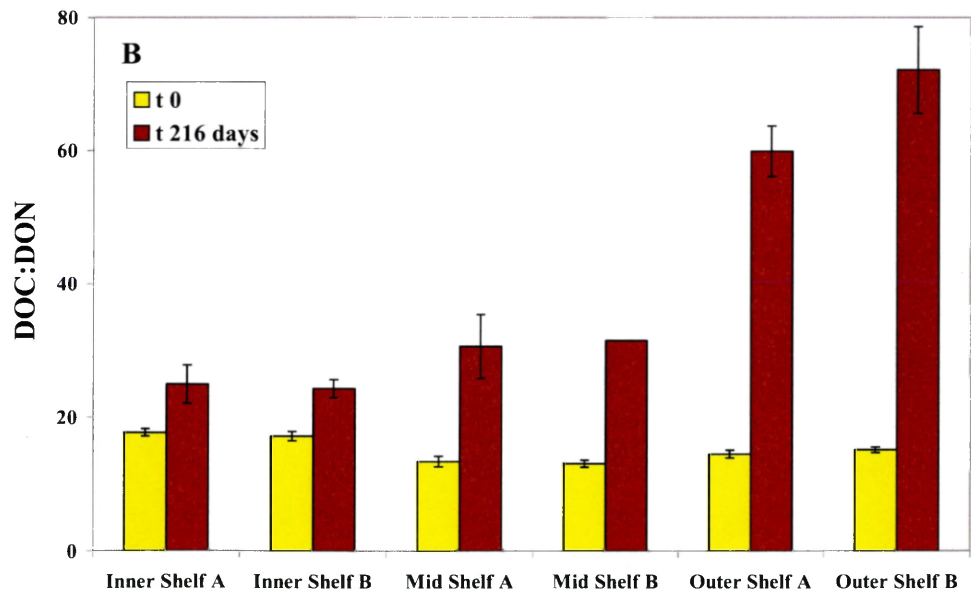


Figure 38. Relationships between A) DIC vs. DOC concentrations and B)  $\delta^{13}\text{C}$ -DIC vs.  $\delta^{13}\text{C}$ -DOC for all surface samples from March, July and October 2005 cruises to the SAB. Lines represent linear correlations between parameters and colors correspond with the three sampling periods.

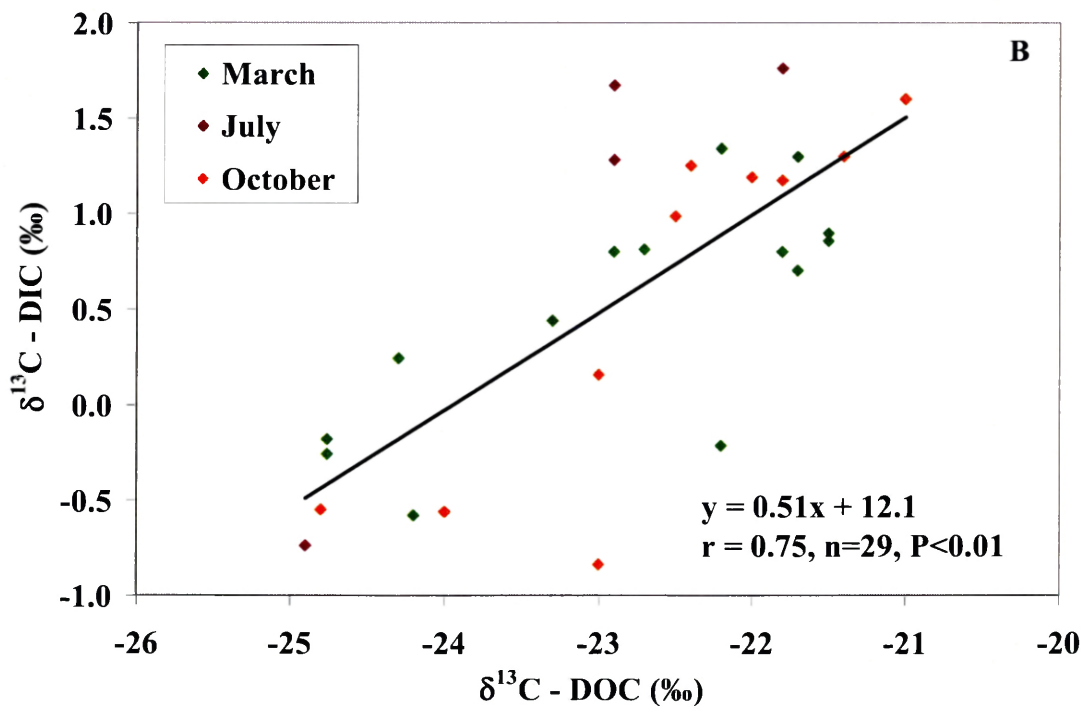
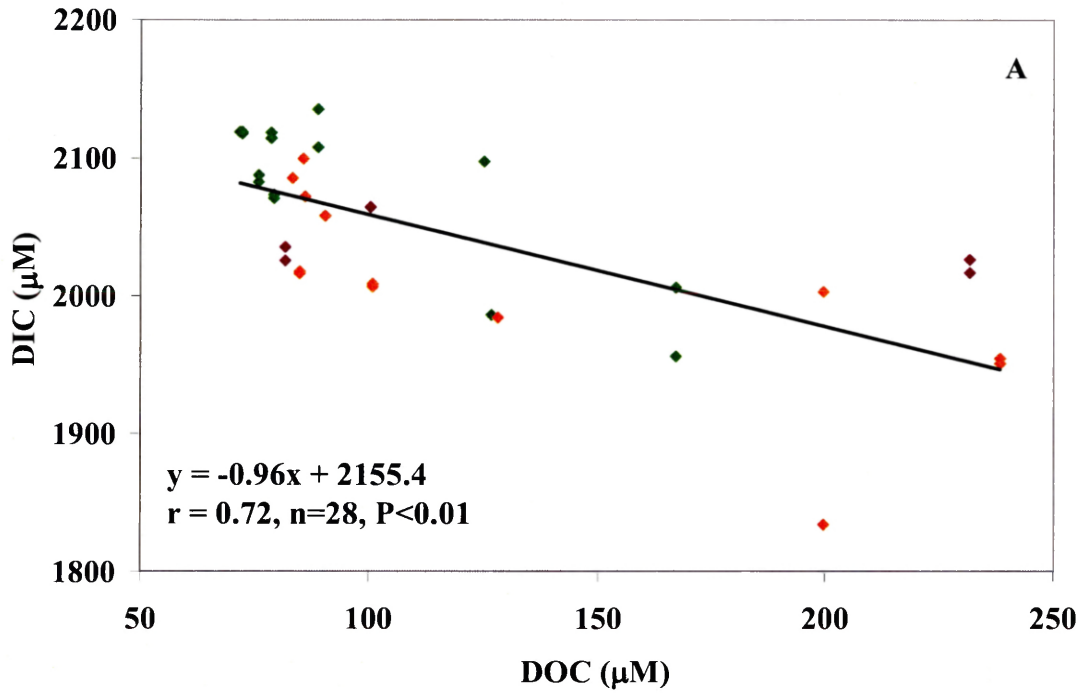
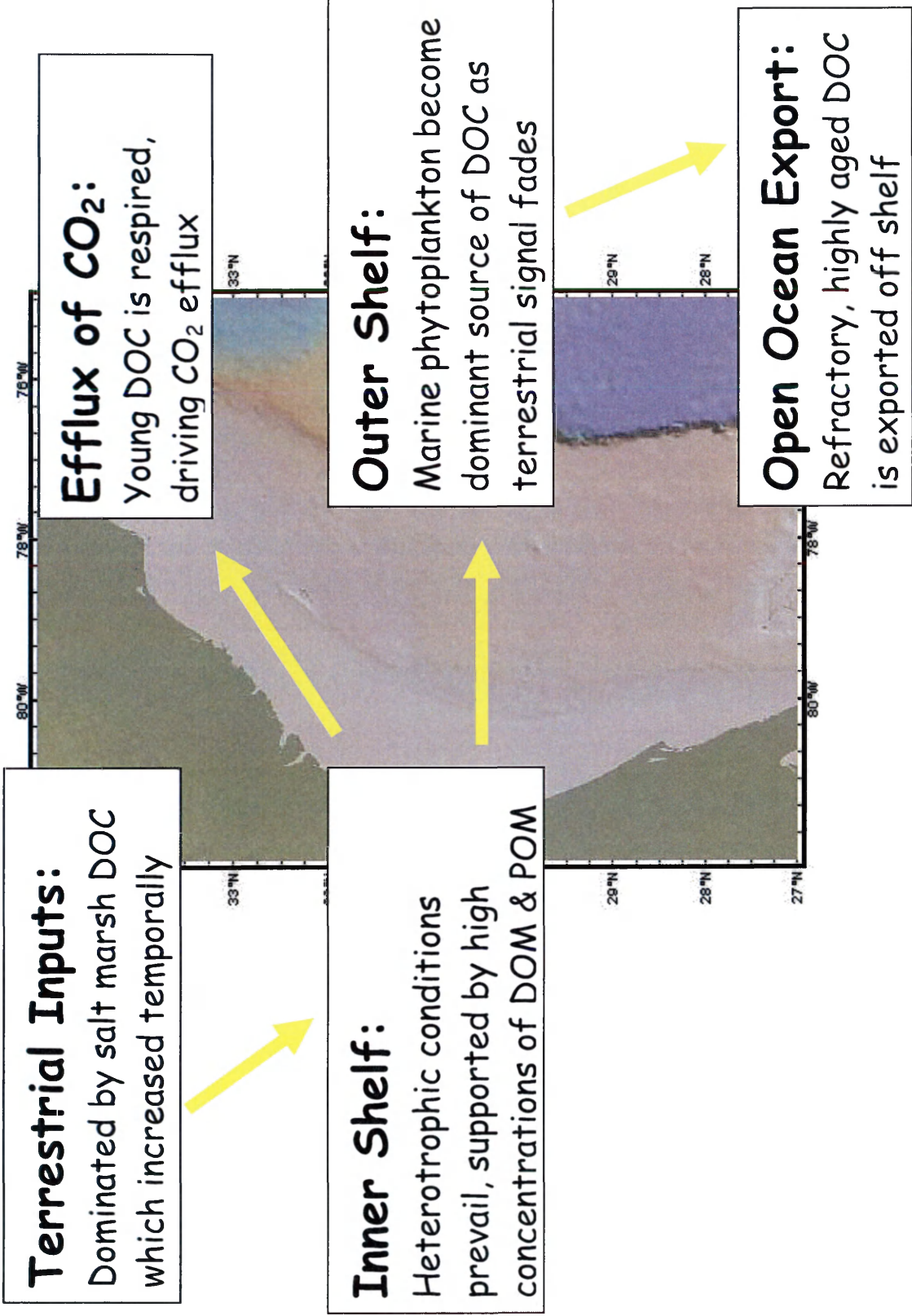


Figure 39. Conceptual Carbon cycling model for the SAB.





**Appendix Table 1. DOC, inorganic and organic nutrient results for all samples from March, July, and October 2005 cruises to the SAB.**

Station	Depth (m)	Date	Bottle	DOC (μM)	NH <sub>4</sub> <sup>+</sup> (μM) <sup>a</sup>	NO <sub>2</sub> <sup>-</sup> +NO <sub>3</sub> <sup>-</sup> (μM)	DIN (μM)	TDN (μM)	DON (μM)	PO <sub>4</sub> <sup>3-</sup> (μM)	TDP (μM)	DOP (μM)	DOC:DON	DON:DOP	DOC:DOP
<i>March 2005 cruise</i>															
A01	2	3/27/2005	A	97.84	0.62	0.00	0.62	6.39	5.77	0.13	0.03	0.00	17.0		
A01	2	3/27/2005	B	101.78	0.62	0.00	0.62	6.51	5.89	0.00	0.03	0.03	17.3	173.7	3002.4
A01	14	3/27/2005	A	100.98	0.62	0.00	0.62	7.92	7.30	0.00	0.05	0.05	13.8	141.7	1960.8
A01	14	3/27/2005	B	101.83	0.62	0.00	0.62	7.91	7.29	0.05	0.03	0.00	14.0		
A04	2	3/27/2005	A	80.82	0.62	0.00	0.62	5.98	5.36	0.02	0.00	0.00	15.1		
A04	2	3/27/2005	B	82.46	0.62	0.00	0.62	5.65	5.03	0.01	0.03	0.01	16.4	359.5	5896.2
A04	30	3/27/2005	A	74.43	0.62	3.11	3.73	8.11	4.39	0.18	0.00	0.00	17.0		
A04	30	3/27/2005	B	72.03	0.62	3.63	4.25	8.44	4.19	0.11	0.00	0.00	17.2		
A08	3	3/27/2005	A	75.22	0.62	0.05	0.67	5.89	5.22	0.00	0.09	0.09	14.4	56.2	809.6
A08	3	3/27/2005	B	75.88	0.62	0.00	0.62	5.95	5.33	0.03	0.00	0.00	14.2		
A08	51	3/27/2005	A	76.15	0.62	0.00	0.62	4.67	4.05	0.13	0.11	0.00	18.8		
A08	51	3/27/2005	B	77.07	0.62	0.00	0.62	5.67	5.05	0.07	0.09	0.02	15.3	246.8	3764.6
A08	151	3/27/2005	A	76.45	0.62	1.68	2.30	12.08	9.78	0.15	0.55	0.40	7.8	24.6	192.4
A08	151	3/27/2005	B	76.74	0.62	1.86	2.48	10.77	8.28	0.12	0.54	0.42	9.3	19.7	182.9
A08	601	3/27/2005	A	51.24	0.62	19.31	19.93	26.75	6.83	1.26	1.53	0.27	7.5	25.1	188.6
A08	601	3/27/2005	B	55.96	0.62	20.30	20.92	27.87	6.95	1.24	1.64	0.40	8.0	17.2	138.3
B01	2	3/26/2005	A	124.30	0.95	0.00	0.95	6.76	5.81	0.13	0.09	0.00	21.4		
B01	2	3/26/2005	B	125.95	0.95	0.00	0.95	7.65	6.70	0.01	0.14	0.13	18.8	50.3	945.4
B01	17	3/26/2005	A	125.85	0.95	0.00	0.95	7.45	6.50	0.05	0.21	0.16	19.4	40.4	782.3
B01	17	3/26/2005	B	126.32	0.95	0.00	0.95	7.42	6.47	0.09	0.12	0.03	19.5	203.4	3972.2
B07	3	3/26/2005	A	78.81	0.95	0.24	1.19	6.90	5.70	0.00	0.10	0.10	13.8	58.6	810.0
B07	3	3/26/2005	B	78.38	0.95	0.39	1.34	6.42	5.08	0.00	0.10	0.10	15.4	49.6	765.4
B07	15	3/26/2005	A	74.02	0.95	1.81	2.76	7.62	4.86	0.19	0.24	0.05	15.2	102.9	1567.6
B07	15	3/26/2005	B	73.99	0.95	1.88	2.83	7.30	4.48	0.02	0.22	0.20	16.5	22.7	375.3

<sup>a</sup> March 2005 NH<sub>4</sub><sup>+</sup> values were averaged by transect to minimize error; the standard deviation of each transect calculated as an estimate of error. These estimated values (concentrations and standard deviations) for NH<sub>4</sub><sup>+</sup> are indicated in italics.

**Appendix Table 1. (cont.)**

B07	38	3/26/2005	B	74.78	0.95	2.32	3.27	8.14	4.87	0.18	0.20	0.02	15.4	312.4	4801.7
B07	38	3/26/2005	A	73.02	0.95	2.32	3.27	8.12	4.85	0.14	0.25	0.11	15.0	46.0	691.8
B11	2	3/26/2005	A	71.57	0.95	2.44	3.39	5.86	2.47	0.01	0.11	0.09	29.0	26.5	766.4
B11	2	3/26/2005	B	72.92	0.95	2.09	3.04	6.86	3.81	0.18	0.06	0.00	19.1		
B11	51	3/26/2005	A	73.36	0.95	0.45	1.40	5.73	4.33	0.03	0.00	0.00	16.9		
B11	51	3/26/2005	B	76.09	0.95	0.18	1.13	5.84	4.71	0.06	0.00	0.00	16.2		
B11	150	3/26/2005	A	72.74	0.95	3.07	4.02	9.57	5.55	0.18	0.25	0.07	13.1	80.5	1055.2
B11	150	3/26/2005	B	70.77	0.95	3.42	4.37	9.55	5.18	0.18	0.23	0.05	13.7	111.0	1515.4
B11	301	3/26/2005	A	56.75	0.95	9.60	10.55	17.73	7.18	0.32	0.85	0.33	7.9	21.8	172.3
B11	301	3/26/2005	B	54.93	0.95	9.99	10.94	18.42	7.49	0.38	0.87	0.29	7.3	25.4	186.6
B11	497	3/26/2005	A	48.80	0.95	16.61	17.56	27.28	9.73	0.95	1.59	0.63	5.0	15.3	76.8
B11	497	3/26/2005	B	50.09	0.95	17.53	18.48	27.38	8.90	1.03	1.66	0.64	5.6	14.0	78.6
B11	630	3/26/2005	A	46.89	0.95	17.73	18.68	28.19	9.51	1.05	1.63	0.58	4.9	16.4	80.9
B11	630	3/26/2005	B	49.64	0.95	17.69	18.64	27.53	8.89	1.03	1.72	0.70	5.6	12.7	71.1
Sapelo R. 1	2	3/23/2005	A		0.71	0.00	0.71	8.75	8.04	0.30	0.07	0.00			
Sapelo R. 1	2	3/23/2005	B		0.71	0.00	0.71	8.83	8.12	0.29	0.09	0.00			
C01	2	3/23/2005	A	168.82	0.71	0.00	0.71	8.67	7.96	0.20	0.19	0.00	21.2		
C01	2	3/23/2005	B	165.77	0.71	0.00	0.71	7.96	7.25	0.27	0.02	0.00	22.9		
C09	3	3/23/2005	A	89.08	0.71	0.00	0.71	5.86	5.15	0.00	0.00	0.00	17.3		
C09	3	3/23/2005	B	88.48	0.71	0.00	0.71	5.50	4.79	0.00	0.00	0.00	18.5		
C09	31	3/23/2005	A	87.05	0.71	0.00	0.71	5.63	4.92	0.12	0.00	0.00	17.7		
C09	31	3/23/2005	B	86.30	0.71	0.00	0.71	5.75	5.04	0.16	0.00	0.00	17.1		
C14	2	3/23/2005	A	79.81	0.71	0.00	0.71	5.45	4.74	0.09	0.00	0.00	16.8		
C14	2	3/23/2005	B	78.64	0.71	0.00	0.71	5.48	4.77	0.14	0.00	0.00	16.5		
C14	50	3/23/2005	A	76.22	0.71	0.93	1.64	6.51	4.87	0.04	0.00	0.00	15.6		
C14	50	3/23/2005	B	76.05	0.71	0.90	1.61	6.69	5.08	0.05	0.00	0.00	15.0		
C14	149	3/23/2005	A	56.93	0.71	7.15	7.86	14.16	6.31	0.37	0.17	0.00	9.0		
C14	149	3/23/2005	B	57.71	0.71	8.13	8.84	14.43	5.59	0.40	0.11	0.00	10.3		
C14	249	3/23/2005	A		0.71	2.98	3.69	9.44	5.75	0.19	0.00	0.00			
C14	249	3/23/2005	B	76.62	0.71	2.50	3.21	8.66	5.45	0.12	0.00	0.00	14.0		
D02	1	3/21/2005	A		0.67	0.00	0.67	6.39	5.72	0.18	0.17	0.00			
D02	1	3/21/2005	B	126.78	0.67	0.00	0.67	7.11	6.44	0.15	0.04	0.00	19.7		

**Appendix Table 1. (cont.)**

D02	9	3/21/2005	A	112.08	0.67	0.19	0.86	6.87	6.02	0.00	0.00	0.00	18.6	
D02	9	3/21/2005	B	112.97	0.67	0.01	0.68	6.84	6.15	0.03	0.00	0.00	18.4	
D07	2	3/21/2005	A	71.08	0.67	0.05	0.72	6.35	5.63	0.01	0.19	0.18	12.6	396.9
D07	2	3/21/2005	B	72.40	0.67	0.15	0.82	5.84	5.02	0.01	0.17	0.16	14.4	456.2
D07	31	3/21/2005	A	71.20	0.67	0.14	0.81	6.49	5.68	0.02	0.27	0.25	12.5	284.1
D07	31	3/21/2005	B	68.82	0.67	0.01	0.68	6.13	5.45	0.02	0.00	0.00	12.6	
D11	2	3/22/2005	A	74.22	0.67	0.04	0.71	5.82	5.11	0.04	0.05	0.01	14.5	8379.1
D11	2	3/22/2005	B	77.45	0.67	0.00	0.67	5.82	5.15	0.07	0.00	0.00	15.0	
D11	26	3/22/2005	A	69.21	0.67	1.34	2.01	7.63	5.62	0.02	0.07	0.04	12.3	131.9
D11	26	3/22/2005	B	67.88	0.67	1.41	2.08	8.10	6.03	0.13	0.23	0.10	11.3	58.8
D11	51	3/22/2005	A	64.47	0.67	2.72	3.39	9.71	6.32	0.19	0.00	0.00	10.2	
D11	51	3/22/2005	B	64.32	0.67	2.76	3.43	9.89	6.46	0.16	0.21	0.05	10.0	1178.0
D11	150	3/22/2005	A	51.97	0.67	10.33	11.00	20.46	9.46	0.36	0.92	0.35	5.5	26.7
D11	150	3/22/2005	B	49.59	0.67	10.81	11.48	21.20	9.72	0.39	0.83	0.24	5.1	40.4
D11	298	3/22/2005	A	44.87	0.67	15.98	16.65	29.77	13.12	0.98	1.55	0.58	3.4	22.7
D11	298	3/22/2005	B	45.74	0.67	16.44	17.11	30.78	13.67	0.98	1.55	0.57	3.3	24.1
D11	381	3/22/2005	A	49.06	0.67	17.11	17.78	31.86	14.07	0.98	1.36	0.38	3.5	37.3
D11	381	3/22/2005	B	44.93	0.67	17.95	18.62	32.25	13.63	1.00	1.22	0.21	3.3	64.4
E01	3	3/20/2005	A	128.16	0.51	0.20	0.71	8.00	7.29	0.00	0.17	0.17	17.6	43.1
E01	3	3/20/2005	B	126.65	0.51	0.22	0.73	6.82	6.09	0.10	0.35	0.25	20.8	757.9
E01	13	3/20/2005	A	126.45	0.51	0.01	0.52	6.51	6.00	0.00	0.22	0.21	21.1	505.5
E01	13	3/20/2005	B		0.51	0.00	0.51	6.59	6.08	0.02	0.22	0.20	30.4	588.2
E07	3	3/20/2005	A	74.42	0.51	0.04	0.55	2.62	2.07	0.04	0.20	0.16	36.0	0.0
E07	3	3/20/2005	B	75.11	0.51	0.00	0.51	2.81	2.30	0.06	0.11	0.04	466.4	13.0
E07	12	3/20/2005	A	76.04	0.51	0.92	1.43	3.08	1.64	0.05	0.18	0.13	32.7	51.2
E07	12	3/20/2005	B		0.51	0.00	0.51	3.57	3.06	0.01	0.22	0.21	46.3	1671.6
E07	30	3/20/2005	A	76.12	0.51	0.00	0.51	4.23	3.72	0.02	0.15	0.13	20.5	567.0
E07	30	3/20/2005	B	77.48	0.51	0.10	0.61	4.71	4.10	0.05	0.14	0.09	14.5	0.0
E11	3	3/20/2005	A	78.87	0.51	0.01	0.52	5.18	4.66	0.00	0.14	0.14	28.9	592.3
E11	3	3/20/2005	B	80.19	0.51	0.00	0.51	5.13	4.62	0.00	0.30	0.30	18.9	855.4
E11	50	3/20/2005	A	73.78	0.51	2.36	2.87	8.79	5.91	0.18	0.49	0.31	16.9	567.4
E11	50	3/20/2005	B		0.51	2.66	3.17	8.32	5.16	0.15	0.36	0.21	17.4	270.2
													12.5	18.8
													24.3	234.3
													0.0	0.0

**Appendix Table 1. (cont.)**

E11	151	3/20/2005	A	56.44	0.51	10.56	11.07	17.43	6.37	0.62	0.69	0.07	8.9	87.0	771.9
E11	151	3/20/2005	B		0.51	11.14	11.65	18.20	6.55	0.57	0.80	0.23		28.9	0.0
E11	300	3/20/2005	A	56.83	0.51	14.44	14.95	20.51	5.56	0.79	1.23	0.43	10.2	12.8	130.8
E11	300	3/20/2005	B	56.40	0.51	14.79	15.30	22.36	7.06	0.84	1.19	0.35	8.0	20.2	161.6
E12	2	3/21/2005	A	80.34	0.53	2.76	3.29	4.27	0.97	0.05	0.07	0.03		33.9	2799.3
E12	2	3/21/2005	B	80.04	0.53	0.16	0.69	3.99	3.31	0.05	0.00	0.00	24.2		
E12	52	3/21/2005	A	79.86	0.53	0.00	0.53	4.50	3.97	0.05	0.27	0.23	20.1	17.6	354.3
E12	52	3/21/2005	B		0.53	0.00	0.53	4.39	3.86	0.00	0.01	0.01		478.0	0.0
E12	101	3/21/2005	A	85.67	0.53	0.04	0.57	5.02	4.45	0.01	0.00	0.00	19.2		
E12	101	3/21/2005	B	77.26	0.53	0.10	0.63	4.62	3.99	0.01	0.00	0.00	19.4		
E12	150	3/21/2005	A	72.98	0.53	0.13	0.66	4.33	3.67	0.08	0.00	0.00	19.9		
E12	150	3/21/2005	B		0.53	0.11	0.64	4.34	3.69	0.03	0.06	0.03		110.1	0.0
E12	500	3/21/2005	A	59.32	0.53	3.21	3.74	8.66	4.92	0.17	0.24	0.07	12.1	70.3	847.9
E12	500	3/21/2005	B	59.45	0.53	3.53	4.06	9.94	5.88	0.17	0.29	0.12	10.1	49.4	499.1
E12	899	3/21/2005	A	52.28	0.53	10.68	11.21	21.21	10.00	0.69	0.94	0.25	5.2	40.4	210.9
E12	899	3/21/2005	B	53.00	0.53	11.40	11.93	22.98	11.05	0.65	1.21	0.56	4.8	19.8	95.0
<i>July/August 2005 cruise</i>															
A01	2	8/3/2005	A	92.26	0.09	0.00	0.09	7.51	7.42	0.12	0.21	0.09	12.4	83.3	1036.5
A01	2	8/3/2005	B		0.66	0.00	0.66	7.76	7.10	0.23	0.12	0.00			
A01	12	8/3/2005	A	100.23	0.26	0.01	0.27	7.95	7.68	0.31	0.43	0.12	13.0	65.0	847.5
A01	12	8/3/2005	B		0.61	0.10	0.71	8.23	7.51	0.31	0.27	0.00			
A04	2	8/3/2005	A	90.28	0.62	0.42	1.04	7.12	6.07	0.07	0.00	0.00	14.9		
A04	2	8/3/2005	B		0.72	0.55	1.27	7.03	5.76	0.12	0.09	0.00			
A04	31	8/3/2005	A	86.01	0.64	0.39	1.03	7.80	6.77	0.09	0.27	0.17	12.7	39.0	496.1
A04	31	8/3/2005	B		0.38	0.60	0.98	7.64	6.66	0.22	0.26	0.05		139.9	0.0
A08	1	8/3/2005	A	84.93	0.62	0.48	1.10	7.16	6.06	0.10	0.09	0.00	14.0		
A08	1	8/3/2005	B		0.36	0.41	0.78	6.75	5.98	0.15	0.06	0.00			
A08	49	8/3/2005	A	79.97	0.64	0.54	1.18	6.89	5.70	0.22	0.03	0.00	14.0		
A08	49	8/3/2005	B		0.46	0.47	0.93	6.53	5.59	0.08	0.12	0.04		129.6	0.0
A08	151	8/3/2005	A	65.45	0.38	2.64	3.02	8.96	5.94	0.31	0.23	0.00	11.0		
A08	151	8/3/2005	B		0.42	2.83	3.25	8.99	5.74	0.30	0.15	0.00			
A08	302	8/3/2005	A	54.15	0.63	15.39	16.02	22.37	6.35	1.08	1.06	0.00	8.5		



**Appendix Table 1. (cont.)**

C15	1	7/30/2005	B	82.16	0.29	0.01	0.29	6.32	6.03	0.21	0.18	0.00	13.6		
C15	50	7/30/2005	A	82.08	0.35	0.21	0.55	6.56	6.00	0.25	0.12	0.00	13.7		
C15	50	7/30/2005	B	85.48	0.19	0.14	0.33	6.68	6.35	0.24	0.24	0.01	13.5	735.1	9892.7
C15	152	7/30/2005	A	67.16	0.42	19.06	19.48	23.89	4.42	1.20	1.32	0.13	15.2	34.8	529.2
C15	152	7/30/2005	B	56.65	0.46	18.98	19.44	23.57	4.13	1.33	1.29	0.00	13.7		
C15	300	7/30/2005	A		0.32	32.18	32.50	34.83	2.33	2.06	1.87	0.00			
C15	300	7/30/2005	B	66.45	0.17	32.07	32.24	36.98	4.74	2.09	2.05	0.00	14.0		
C15	454	7/30/2005	A	52.11	0.34	32.50	32.84	36.29	3.45	2.23	1.96	0.00	15.1		
C15	454	7/30/2005	B	54.29	0.27	32.92	33.19	35.63	2.44	2.13	2.04	0.00	22.3		
D02	2	7/29/2005	A	112.58	0.36	2.47	2.83	9.51	6.68	0.19	0.19	0.00	16.9		
D02	2	7/29/2005	B	116.10	0.23	0.00	0.23	9.54	9.31	0.23	0.30	0.07	12.5	130.7	1629.8
D02	8	7/29/2005	A	115.72	0.36	0.00	0.36	8.44	8.07	0.24	0.29	0.05	14.3	152.4	2183.5
D02	8	7/29/2005	B	116.27	0.25	0.00	0.25	8.77	8.51	0.22	0.32	0.10	13.7	82.0	1120.1
D07	1	7/29/2005	A	134.54	0.38	0.00	0.38	9.53	9.16	0.20	0.28	0.08	14.7	114.7	1686.1
D07	1	7/29/2005	B	134.76	0.35	0.00	0.35	9.43	9.07	0.18	0.16	0.00	14.9		
D07	37	7/29/2005	A	78.37	0.36	0.25	0.61	7.48	6.87	0.31	0.26	0.00	11.4		
D07	37	7/29/2005	B	74.10	0.39	0.67	1.06	7.30	6.24	0.25	0.28	0.03	11.9	186.6	2215.7
D11	2	7/29/2005	A	82.06	0.41	0.00	0.41	6.63	6.22	0.13	0.11	0.00	13.2		
D11	2	7/29/2005	B	81.84	0.26	0.00	0.26	6.65	6.39	0.10	0.01	0.00	12.8		
D11	51	7/29/2005	A	80.56	0.36	0.00	0.36	5.90	5.54	0.20	0.00	0.00	14.5		
D11	51	7/29/2005	B	80.52	0.45	0.00	0.45	6.24	5.80	0.12	0.16	0.04	13.9	143.5	1993.8
D11	151	7/29/2005	A	66.88	0.32	5.24	5.56	11.12	5.56	0.42	0.37	0.00	12.0		
D11	151	7/29/2005	B	62.56	0.18	5.79	5.97	11.38	5.41	0.37	0.32	0.00	11.6		
D11	298	7/29/2005	A	47.76	0.14	27.16	27.30	30.75	3.44	1.83	1.61	0.00	13.9		
D11	298	7/29/2005	B	47.95	0.36	27.75	28.11	30.90	2.79	1.83	1.63	0.00	17.2		
D11	375	7/29/2005	A	51.62	0.28	29.58	29.85	32.65	2.79	2.03	1.72	0.00	18.5		
D11	375	7/29/2005	B	50.44	0.25	29.95	30.20	32.70	2.50	2.06	1.66	0.00	20.2		
E01	2	7/28/2005	A	123.59	1.16	0.00	1.16	9.28	8.12	0.25	0.31	0.07	15.2	121.0	1840.8
E01	2	7/28/2005	B	124.35	0.77	0.00	0.77	9.16	8.39	0.17	0.30	0.14	14.8	61.9	917.5
E01	10	7/28/2005	A	118.39	0.27	0.00	0.27	7.83	7.57	0.16	0.21	0.04	15.6	169.0	2643.9
E01	10	7/28/2005	B	122.47	0.84	0.06	0.90	8.65	7.75	0.12	0.21	0.09	15.8	81.9	1294.1
E07	2	7/28/2005	A	96.16	0.93	0.10	1.03	6.70	5.67	0.20	0.17	0.00	17.0		

**Appendix Table 1. (cont.)**

E07	2	7/28/2005	B	95.16	0.51	0.00	0.51	6.89	6.37	0.16	0.15	0.00	14.9	
E07	31	7/28/2005	A	91.89	0.45	0.00	0.45	6.39	5.94	0.21	0.15	0.00	15.5	
E07	31	7/28/2005	B	87.68	0.65	0.00	0.65	6.03	5.38	0.14	0.06	0.00	16.3	
E11	1	7/28/2005	A	104.51	0.96	0.00	0.96	6.67	5.70	0.03	0.10	0.07	18.3	85.7
E11	1	7/28/2005	B	105.34	0.88	0.00	0.88	7.06	6.18	0.11	0.17	0.05	17.0	121.0
E11	51	7/28/2005	A	84.45	0.99	0.14	1.13	6.31	5.18	0.06	0.15	0.09	16.3	56.6
E11	51	7/28/2005	B	80.99	0.87	0.13	1.00	6.49	5.49	0.07	0.24	0.17	14.7	31.9
E11	149	7/28/2005	A	63.77	0.82	23.41	24.23	26.38	2.15	1.41	1.16	0.00	29.6	
E11	149	7/28/2005	B	60.70	0.44	23.96	24.39	27.12	2.73	1.47	1.23	0.00	22.2	
E11	300	7/28/2005	A	57.14	0.83	30.13	30.96	32.75	1.79	1.92	1.62	0.00	31.9	
E11	300	7/28/2005	B	56.47	0.74	30.49	31.23	32.64	1.41	1.96	1.73	0.00	40.0	
E11	453	7/28/2005	A	62.13	0.39	27.10	27.49	30.28	2.79	1.75	1.45	0.00	22.3	
E11	453	7/28/2005	B	57.96	0.74	27.31	28.06	29.57	1.52	1.79	1.44	0.00	38.2	
T07	2	8/4/2005	A	89.48	0.28	0.00	0.28	7.01	6.73	0.27	0.22	0.00	13.3	
T07	2	8/4/2005	B	91.32	0.48	0.00	0.48	5.87	5.39	0.15	0.16	0.01	16.9	7415.9
T07	51	8/4/2005	A	85.04	0.20	0.00	0.20	6.03	5.83	0.22	0.12	0.00	14.6	
T07	51	8/4/2005	B	83.95	0.51	0.07	0.58	6.28	5.70	0.31	0.15	0.00	14.7	
T07	151	8/4/2005	A	75.18	0.53	1.51	2.04	7.18	5.14	0.17	0.23	0.06	14.6	1290.6
T07	151	8/4/2005	B	76.11	0.46	1.44	1.91	7.28	5.37	0.34	0.13	0.00	14.2	
T07	301	8/4/2005	A	69.11	0.68	2.71	3.39	7.46	4.08	0.14	0.20	0.06	17.0	1145.5
T07	301	8/4/2005	B	65.80	0.25	2.68	2.93	8.92	6.00	0.26	0.25	0.00	11.0	
T07	498	8/4/2005	A	63.80	0.31	12.30	12.61	17.53	4.91	0.98	0.62	0.00	13.0	
T07	498	8/4/2005	B	62.61	0.67	12.11	12.79	16.77	3.98	0.92	0.65	0.00	15.7	
T07	989	8/4/2005	A	60.79	0.45	19.44	19.89	24.15	4.26	1.55	1.22	0.00	14.3	
T07	989	8/4/2005	B	58.38	0.54	19.70	20.24	25.06	4.82	1.54	1.24	0.00	12.1	

*October 2005 cruise*

A01	0	10/15/2005	A	152.34	0.57	1.21	1.78	12.57	10.79	0.51	0.61	0.10	14.1	106.8	1507.4
A01	0	10/15/2005	B	149.83	0.70	1.23	1.93	12.68	10.75	0.42	0.52	0.10	13.9	109.7	1529.3
A01	12	10/15/2005	A	151.44	0.72	1.76	2.48	13.92	11.44	0.47	0.58	0.10	13.2	113.6	1503.4
A01	12	10/15/2005	B	149.43	0.50	2.11	2.61	13.06	10.46	0.44	0.47	0.03	14.3	324.5	4637.5
A04	0	10/15/2005	A	118.28	0.65	0.45	1.10	10.77	9.68	0.28	0.29	0.01	12.2	850.4	10391.6
A04	0	10/15/2005	B	117.88	0.61	0.38	0.99	10.37	9.38	0.19	0.29	0.10	12.6	91.0	1143.4

**Appendix Table 1. (cont.)**

A04	29	10/15/2005	A	113.90	0.98	1.00	1.98	10.45	8.46	0.25	0.41	0.16	13.5	53.4	718.3
A04	29	10/15/2005	B	114.52	0.74	0.94	1.69	11.05	9.37	0.06	0.36	0.30	12.2	31.4	383.3
A08	0	10/15/2005	A	81.12	0.64	0.00	0.64	7.14	6.50	0.07	0.07	0.00	12.5		
A08	0	10/15/2005	B	79.71	0.63	0.00	0.63	6.97	6.34	0.16	0.16	0.00	12.6	3913.3	49219.0
A08	50	10/15/2005	A	77.85	0.27	0.00	0.27	5.94	5.66	0.17	0.13	0.00	13.7		
A08	50	10/15/2005	B	80.14	0.50	0.00	0.50	6.42	5.92	0.05	0.20	0.16	13.5	37.8	511.9
A08	150	10/15/2005	A	61.92	0.55	4.07	4.62	10.42	5.80	0.35	0.28	0.00	10.7		
A08	150	10/15/2005	B	62.81	0.54	4.62	5.16	10.42	5.26	0.35	0.33	0.00	11.9		
A08	302	10/15/2005	A	54.10	0.50	13.81	14.31	19.75	5.44	0.88	0.82	0.00	9.9		
A08	302	10/15/2005	B	55.35	0.49	13.84	14.33	20.01	5.68	0.94	0.79	0.00	9.7		
A08	500	10/15/2005	A	50.80	0.45	27.85	28.30	33.66	5.35	1.83	1.80	0.00	9.5		
A08	500	10/15/2005	B	52.16	0.29	27.69	27.98	34.77	6.79	1.82	1.91	0.08	7.7	82.8	636.3
A08	758	10/15/2005	A	49.68	0.53	29.56	30.09	37.45	7.36	2.03	1.95	0.00	6.8		
A08	758	10/15/2005	B	48.72	0.56	29.56	30.13	36.17	6.04	2.01	2.04	0.03	8.1	209.0	1687.0
B01	2	10/14/2005	A	200.95	0.46	0.70	1.17	13.86	12.69	0.66	0.79	0.13	15.8	98.1	1533.5
B01	2	10/14/2005	B	198.56	0.54	1.39	1.93	14.12	12.19	0.61	0.69	0.09	16.3	140.8	2292.2
B01	14	10/14/2005	A	171.93	0.60	1.70	2.29	12.64	10.35	0.56	0.65	0.09	16.6	114.9	1909.1
B01	14	10/14/2005	B	167.70	0.62	1.70	2.31	13.22	10.90	0.55	0.61	0.06	15.4	177.7	2732.5
B07	1	10/14/2005	A	86.24	0.35	0.17	0.52	7.90	7.37	0.30	0.14	0.00	11.7		
B07	1	10/14/2005	B	85.05	0.25	0.08	0.33	7.42	7.09	0.15	0.21	0.06	12.0	123.1	1476.9
B07	36	10/14/2005	A	86.97	0.23	0.20	0.43	8.42	7.99	0.13	0.17	0.04	10.9	226.8	2468.2
B07	36	10/14/2005	B	86.66	0.20	0.21	0.41	8.99	8.59	0.14	0.21	0.07	10.1	116.3	1174.0
B11	1	10/15/2005	A	82.56	0.16	0.00	0.16	6.23	6.06	0.20	0.05	0.00	13.6		
B11	1	10/15/2005	B	84.16	0.31	0.00	0.31	6.23	5.92	0.24	0.18	0.00	14.2		
B11	51	10/15/2005	A	82.37	0.24	0.00	0.24	6.26	6.02	0.18	0.09	0.00	13.7		
B11	51	10/15/2005	B	84.74	0.26	0.00	0.26	6.15	5.89	0.21	0.13	0.00	14.4		
B11	152	10/15/2005	A	58.21	0.24	6.45	6.69	11.41	4.72	0.49	0.35	0.00	12.3		
B11	152	10/15/2005	B	60.09	0.19	6.74	6.93	12.00	5.07	0.47	0.35	0.00	11.8		
B11	300	10/15/2005	A	53.54	0.40	12.27	12.67	18.16	5.49	0.81	0.73	0.00	9.8		
B11	300	10/15/2005	B	53.92	0.17	12.65	12.83	18.05	5.22	0.87	0.70	0.00	10.3		
B11	499	10/15/2005	A	49.75	0.32	28.87	29.19	34.29	5.09	1.89	1.90	0.01	9.8	555.8	5427.7
B11	499	10/15/2005	B	49.23	0.29	30.03	30.32	35.22	4.90	1.86	1.87	0.01	10.1	467.1	4695.3



**Appendix Table 1. (cont.)**

B11	625	10/15/2005	A	47.99	0.24	30.15	30.39	34.97	4.58	2.00	1.93	0.00	10.5	
B11	625	10/15/2005	B	47.86	0.19	30.29	30.48	35.50	5.02	1.95	1.90	0.00	9.5	
C01	2	10/11/2005	A	238.00	0.57	4.35	4.91	18.39	13.47	1.00	1.11	0.11	17.7	2108.3
C01	2	10/11/2005	B	238.73	0.52	4.81	5.33	18.75	13.42	1.00	1.16	0.16	17.8	1461.4
C09	1	10/12/2005	A	102.13	0.28	0.00	0.28	6.60	6.32	0.30	0.30	0.00	16.2	
C09	1	10/12/2005	B	99.41	0.23	0.00	0.23	7.41	7.18	0.18	0.24	0.05	13.8	1816.5
C09	27	10/12/2005	A	97.97	0.21	0.00	0.21	7.69	7.47	0.21	0.22	0.01	13.1	
C09	27	10/12/2005	B	98.39	0.22	0.00	0.22	7.49	7.27	0.21	0.19	0.00	13.5	7036.4
C15	2	10/14/2005	A	83.70	0.15	0.00	0.15	5.85	5.70	0.29	0.12	0.00	14.7	
C15	2	10/14/2005	B	86.00	0.34	0.00	0.34	6.01	5.68	0.26	0.14	0.00	15.2	
C15	51	10/14/2005	A	84.15	0.18	0.00	0.18	6.10	5.92	0.29	0.17	0.00	14.2	
C15	51	10/14/2005	B	82.21	0.34	0.00	0.34	5.68	5.33	0.28	0.05	0.00	15.4	
C15	149	10/14/2005	A	65.56	0.30	4.76	5.06	9.63	4.57	0.39	0.26	0.00	14.3	
C15	149	10/14/2005	B	64.15	0.18	4.95	5.13	9.85	4.72	0.44	0.29	0.00	13.6	
C15	298	10/14/2005	A	56.32	0.27	19.00	19.27	22.57	3.30	1.23	1.06	0.00	17.1	
C15	298	10/14/2005	B	59.42	0.27	19.15	19.42	22.92	3.50	1.15	1.05	0.00	17.0	
C15	466	10/14/2005	A	54.59	0.31	30.07	30.38	32.99	2.61	1.99	1.71	0.00	20.9	
C15	466	10/14/2005	B	51.04	0.16	30.98	31.14	33.22	2.08	2.11	1.76	0.00	24.5	
D02	-1	10/10/2005	A	127.65	0.33	0.29	0.62	8.33	7.71	0.27	0.26	0.00	16.5	
D02	-1	10/10/2005	B	128.61	0.39	0.14	0.52	9.47	8.94	0.31	0.30	0.00	14.4	
D02	6	10/10/2005	A	123.45	0.45	0.40	0.85	10.52	9.67	0.31	0.35	0.04	12.8	3366.6
D02	6	10/10/2005	B	135.03	0.35	0.67	1.02	10.23	9.21	0.26	0.18	0.00	14.7	
D07	0	10/10/2005	A	91.39	0.20	0.00	0.20	6.71	6.51	0.07	0.24	0.17	14.0	538.0
D07	0	10/10/2005	B	89.54	0.28	0.00	0.28	6.49	6.21	0.20	0.08	0.00	14.4	
D07	37	10/10/2005	A	86.60	0.28	0.38	0.66	6.72	6.05	0.20	0.19	0.00	14.3	
D07	37	10/10/2005	B	86.20	0.25	0.41	0.66	6.85	6.19	0.12	0.20	0.08	13.9	1041.3
D11	0	10/10/2005	A	86.04	0.14	0.22	0.36	7.06	6.70	0.16	0.21	0.05	12.8	1714.8
D11	0	10/10/2005	B		0.27	0.14	0.41	6.37	5.96	0.08	0.22	0.14	42.0	0.0
D11	50	10/10/2005	A	85.73	0.27	0.00	0.27	6.22	5.95	0.22	0.13	0.00	14.4	
D11	50	10/10/2005	B	87.29	0.33	0.00	0.33	6.46	6.13	0.15	0.20	0.05	14.2	1779.1
D11	151	10/10/2005	A	59.37	0.20	17.82	18.02	21.80	3.79	1.18	1.03	0.00	15.7	
D11	151	10/10/2005	B	59.52	0.17	18.33	18.51	22.03	3.52	1.21	1.06	0.00	16.9	

**Appendix Table 1. (cont.)**

D11	300	10/10/2005	A	58.29	0.07	29.23	29.31	31.78	2.47	2.00	1.66	0.00	23.6
D11	300	10/10/2005	B	64.69	0.14	29.98	30.13	32.39	2.26	2.04	1.91	0.00	28.6
D11	392	10/10/2005	A	53.52	0.19	30.12	30.31	33.54	3.23	2.05	1.75	0.00	16.6
D11	392	10/10/2005	B	51.75	0.36	29.47	29.84	33.22	3.38	2.07	1.89	0.00	15.3
E01	0	10/8/2005	A	132.05	1.34	0.47	1.81	11.72	9.92	0.31	0.40	0.09	13.3
E01	0	10/8/2005	B	130.51	1.26	0.34	1.60	11.49	9.89	0.36	0.35	0.00	13.2
E01	8	10/8/2005	A	129.59	1.32	0.49	1.81	10.64	8.83	0.30	0.34	0.04	14.7
E01	8	10/8/2005	B	131.47	1.43	0.76	2.18	10.77	8.59	0.34	0.36	0.02	15.3
E07	1	10/9/2005	A	79.66	0.73	0.22	0.95	6.35	5.40	0.24	0.15	0.00	14.7
E07	1	10/9/2005	B	80.27	0.70	0.00	0.69	6.57	5.87	0.19	0.17	0.00	13.7
E07	27	10/9/2005	A	79.04	0.64	0.43	1.07	6.92	5.86	0.18	0.14	0.00	13.5
E07	27	10/9/2005	B	77.55	0.69	0.32	1.01	6.59	5.58	0.13	0.05	0.00	13.9
E11	0	10/9/2005	A	75.56	0.50	0.36	0.86	6.59	5.73	0.27	0.13	0.00	13.2
E11	0	10/9/2005	B	76.92	0.60	0.00	0.60	6.47	5.87	0.19	0.02	0.00	13.1
E11	50	10/9/2005	A	69.20	0.61	1.72	2.32	8.09	5.77	0.36	0.17	0.00	12.0
E11	50	10/9/2005	B	69.97	0.53	1.98	2.51	8.61	6.11	0.29	0.11	0.00	11.5
E11	150	10/9/2005	A	50.00	0.52	20.98	21.50	24.43	2.93	1.37	1.10	0.00	17.1
E11	150	10/9/2005	B	53.74	0.52	21.41	21.93	25.41	3.49	1.42	1.12	0.00	15.4
E11	299	10/9/2005	A	49.43	0.54	29.42	29.95	32.96	3.01	1.95	1.75	0.00	16.4
E11	299	10/9/2005	B	47.63	0.30	30.35	30.66	34.62	3.97	2.06	1.75	0.00	12.0
E11	438	10/9/2005	A	47.69	0.30	30.30	30.59	33.62	3.02	2.02	1.71	0.00	15.8
E11	438	10/9/2005	B	48.00	0.59	30.30	30.89	33.84	2.95	1.83	1.68	0.00	16.2
T07a	2	10/16/2005	A	78.51	0.31	0.00	0.31	5.56	5.25	0.16	0.15	0.00	14.9
T07a	2	10/16/2005	B	84.89	0.25	0.00	0.25	6.11	5.87	0.16	0.09	0.00	14.5
T07a	51	10/16/2005	A	88.33	0.36	0.00	0.36	5.25	4.90	0.17	0.21	0.04	18.0
T07a	51	10/16/2005	B	85.70	0.23	0.00	0.23	5.60	5.36	0.16	0.09	0.00	16.0
T07a	151	10/16/2005	A	82.15	0.19	0.00	0.19	6.08	5.90	0.15	0.10	0.00	13.9
T07a	151	10/16/2005	B	79.88	0.25	0.00	0.25	5.71	5.47	0.19	0.08	0.00	14.6
T07a	301	10/16/2005	A	60.43	0.27	3.00	3.27	8.08	4.82	0.28	0.16	0.00	12.5
T07a	301	10/16/2005	B	60.31	0.20	3.07	3.27	7.87	4.60	0.32	0.31	0.00	13.1
T07a	501	10/16/2005	A	55.47	0.13	7.25	7.38	11.52	4.13	0.47	0.43	0.00	13.4
T07a	501	10/16/2005	B	55.33	0.12	7.45	7.56	11.73	4.17	0.49	0.47	0.00	13.3

**Appendix Table 1. (cont.)**

	899	10/16/2005	A	50.35	0.27	21.01	21.28	25.04	3.76	1.29	1.39	0.09	13.4	39.8	533.3
T07a	899	10/16/2005	B	52.28	0.33	21.00	21.32	25.14	3.82	1.37	1.37	0.00	13.7		

**Appendix Table 2. DOM dark decomposition final DOC and nutrient results for July and October 2005 experiments.**  
 Note that no DOC:DOP or DON:DOP ratios are reported because DOP was below detection in all final samples.

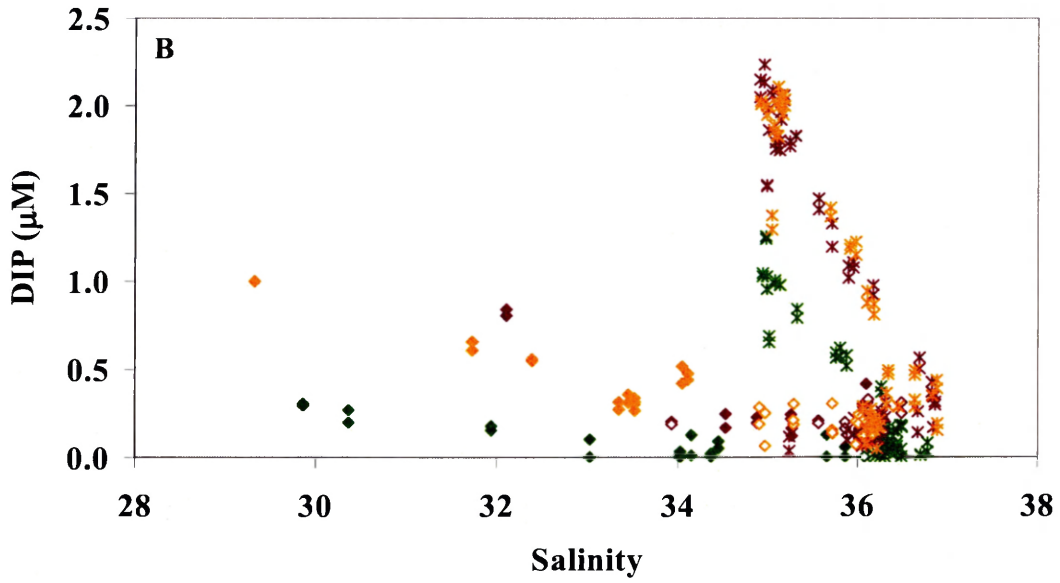
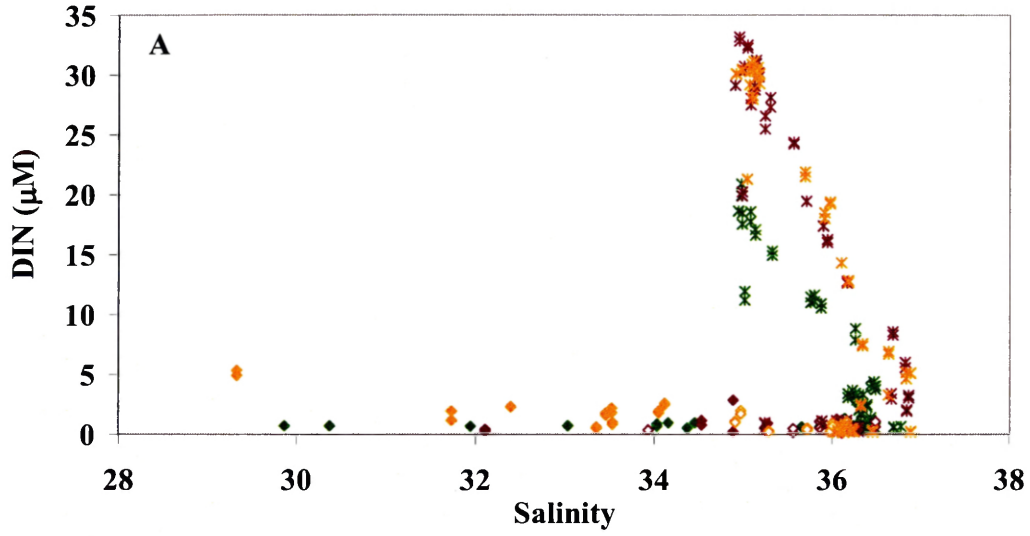
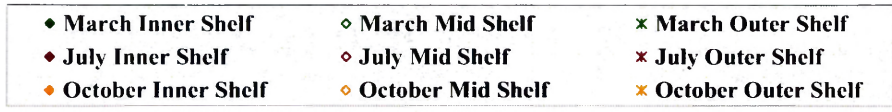
Station	Sample Depth (m)	Bottle	DOC (µM)	NH <sub>4</sub> <sup>+</sup> (µM)	NO <sub>2</sub> <sup>-</sup> +NO <sub>3</sub> <sup>-</sup> (µM)	TDN (µM)	DON (µM)	PO <sub>4</sub> <sup>3-</sup> (µM)	TDP (µM)	DOP (µM)	DOC:DON
<i>Summer Dark Incubation</i>											
Inner Shelf A	2	A	213.79	0.94	5.07	12.61	6.61	1.57	0.98	0.00	32.4
	2	B	211.56	1.12	4.52	12.08	6.44	1.45	1.05	0.00	32.8
Inner Shelf B	2	A	212.74	1.14	5.46	12.52	5.92	1.55	1.25	0.00	36.0
	2	B	211.06	0.96	5.59	12.47	5.93	1.60	0.93	0.00	35.6
Mid Shelf A	2	A	112.85	0.66	1.67	5.20	2.87	0.56	0.04	0.00	39.3
	2	B	109.98	1.03	1.89	5.26	2.34	0.53	0.13	0.00	47.0
Mid Shelf B	2	A	89.10	0.72	1.97	4.14	1.46	0.42	0.00	0.00	61.2
	2	B	100.72	0.57	2.25	5.83	3.00	0.48	0.17	0.00	33.5
Outer Shelf A	2	A	159.09	0.48	0.98	2.56	1.10*	0.42	0.00	0.00	145.0*
	2	B	164.11	0.21	0.75	3.11	2.15	0.38	0.02	0.00	76.3
Outer Shelf B	2	A	86.40	0.79	0.77	4.05	2.49	0.44	0.00	0.00	34.7
	2	B	79.24	0.75	0.73	3.80	2.32	0.41	0.00	0.00	34.2
<i>Fall Dark Incubation</i>											
Inner Shelf A	2	A	197.61	0.73	7.67	17.13	8.73	1.62	1.03	0.00	22.6
	2	B	194.98	0.56	8.60	16.28	7.12	1.54	0.96	0.00	27.4
Inner Shelf B	2	A	194.92	0.63	8.26	17.06	8.16	1.57	1.03	0.00	23.9
	2	B	191.76	0.54	8.24	16.47	7.69	1.58	1.04	0.00	24.9
Mid Shelf A	2	A	90.56	0.32	2.44	5.42	2.66	0.52	0.07	0.00	34.1
	2	B	88.22	0.46	1.82	5.49	3.21	0.51	0.06	0.00	27.4
Mid Shelf B	2	A	88.77	0.70	2.12	5.63	2.81	0.48	0.00	0.00	31.6
	2	B	80.34	0.94	2.83	5.03	1.26	0.46	0.00	0.00	63.7
Outer Shelf A	2	A	207.94	0.42	0.52	4.64	3.70	0.25	0.00	0.00	56.2
	2	B	215.15	0.43	0.54	4.35	3.38	0.29	0.00	0.00	63.7
Outer Shelf B	2	A	235.01	0.59	0.11	3.67	2.97	0.28	0.00	0.00	79.0
	2	B	233.58	0.30	0.00	3.68	3.38	0.26	0.00	0.00	69.1

\* Result is considered an outlier and not included in results.

**Appendix Table 3. Inorganic and organic nutrient results for river, estuarine, and salt marsh end members from July 2006.**

Site	Sample Date	Bottle	POC (µg/L)	DOC (µM)	NH <sub>4</sub> <sup>+</sup> (µM)	NO <sub>2</sub> <sup>-</sup> + NO <sub>3</sub> <sup>-</sup> (µM)	TDN (µM)	DON (µM)	PO <sub>4</sub> <sup>3-</sup> (µM)	TDP (µM)	DOP (µM)	DOC: DON	DON: DOP	DOC: DOP
St Johns River, FL	7/11/2006	A		956.07	0.53	9.76	45.51	35.22	3.16	3.28	0.12	27.1	284.7	7726.8
	7/11/2006	B		977.00	0.53	11.02	46.19	34.64	3.01	2.99	0.00	28.2		
Altamaha River, GA	7/11/2006	A	2337	427.74	0.93	4.31	22.61	17.36	1.00	1.43	0.43	24.6	40.3	992.0
	7/11/2006	B		425.50	0.93	4.20	19.58	14.45	0.98	1.05	0.07	29.5	200.1	5894.8
Hudson Creek, GA	7/11/2006	A	1352	453.77	0.87	0.14	21.65	20.65	1.80	1.88	0.08	22.0	248.1	5453.5
	7/11/2006	B		447.79	0.86	0.21	23.06	21.99	1.87	1.63	0.00	20.4		
Sapelo River, GA	7/11/2006	A	1858	994.56	1.02	0.11	43.81	42.69	6.12	5.38	0.00	23.3		
	7/11/2006	B	1950	955.84	0.90	0.09	41.59	40.60	6.99	5.35	0.00	23.5		
Savannah River, GA	7/12/2006	A	1028	241.51	2.70	27.74	44.00	13.56	1.95	2.02	0.07	17.8	186.3	3318.3
	7/12/2006	B	1051	255.88	2.73	27.67	44.20	13.79	1.84	2.03	0.19	18.5	72.0	1335.9
Cooper River, SC	7/12/2006	A		240.91	1.72	1.68	15.39	12.00	1.31	1.13	0.00	20.1		
	7/12/2006	B		226.82	1.78	1.82	14.87	11.27	1.33	1.07	0.00	20.1		
Great Pee Dee River, SC	7/12/2006	A	511	1123.60	1.36	13.83	54.67	39.48	1.06	2.07	1.00	28.5	39.3	1119.4
	7/12/2006	B		1176.16	1.51	14.21	53.63	37.90	1.09	1.98	0.89	31.0	42.5	1318.2
Cape Fear River, NC	7/13/2006	A		938.09	4.43	32.93	65.28	27.93	2.36	2.95	0.59	33.6	47.1	1582.6
	7/13/2006	B		939.87	4.58	34.90	65.66	26.18	2.75	2.68	0.00	35.9		

Appendix Figure 1. Distributions of A) total dissolved inorganic nitrogen (DIN) and B) dissolved inorganic phosphorus (DIP) as a function of salinity for March, July, and October 2005 cruises to the SAB.



## VITA

Born in Newport News, VA, November 9, 1976. Attended University of Rhode Island, Kingston, RI and graduated in 1999 with a B.S. in Marine Biology. Worked and traveled for several years before entering the M.S. program of the School of Marine Science in August 2004.