Limnol. Oceanogr., 49(2), 2004, 341–354

Carbon dioxide degassing and inorganic carbon export from a marsh-dominated estuary (the Duplin River): A marsh CO_2 pump

Zhaohui Aleck Wang[1] *and Wei-Jun Cai*[2]
Department of Marine Sciences, University of Georgia, Athens, Georgia 30602

Abstract

We investigated the seasonal changes and the interactions of the CO_2 system in a marsh-dominated estuary, the Duplin River, on Sapelo Island, Georgia. Surface water $p\mathrm{CO_2}$, total alkalinity (TA), and total dissolved inorganic carbon (DIC) showed a pronounced seasonal progression in this system. The estuary released 256–306 g C m^{-2} (of water) yr^{-1} of CO_2 to the atmosphere and exported 109 g C m^{-2} (of water) yr^{-1} of DIC to adjacent coastal waters. There was a clear seasonal pattern in both fluxes with spring minima, and late summer and fall maxima. Release of inorganic carbon as a respiratory product from surrounding salt marshes is the primary process supporting these two carbon export terms. Concurrently, TA was exported from the Duplin River mainly in summer and fall as a result of anaerobic respiration in marshes. Based on data from the upper Duplin River, export of inorganic carbon from salt marshes was 156 g C m^{-2} (of marsh) yr^{-1}. Extrapolation of this value to all southeastern U.S. salt marshes indicates that they cumulatively export 0.7×10^{12} g inorganic carbon annually to coastal waters. This export rivals that of riverine inorganic carbon flux. We propose that the CO_2 fixation of marsh grasses and the subsequent export of inorganic and organic carbon is one major mechanism that causes the marsh-influenced nearshore and offshore waters in the southeastern U.S. to be annual net sources of atmospheric CO_2. We also suggest that this process provides an efficient and unique means for ocean carbon sequestration of atmospheric CO_2.

The marsh-influenced estuaries, tidal creeks, and coastal waters adjacent to Sapelo Island, Georgia, have been the subjects of pioneer ecological studies on marsh–water interaction since the 1950s (e.g., Ragotzkie and Bryson 1955; Teal 1962; Odum 1968). Based on studies in the Sapelo marshes, it was proposed that intertidal marshes are a net source of organic matter and nutrients that fertilize adjacent estuarine and coastal waters (Teal 1962; Odum 1968). For decades this controversial outwelling hypothesis has fascinated the scientific community and triggered intensive debate (e.g., Nixon 1980; Wiegert et al. 1981; Chalmers et al. 1985; Hopkinson 1985; Dame et al. 1986; Dame 1994; Childers et al. 2000). The current paradigm is that marsh–estuary interaction of a particular system is inherently complicated and depends on climatological, biogeochemical, and hydrological factors such as geological age, developmental status, and tidal range (Childers 1994; Dame 1994). Consequently, the outwelling hypothesis should be viewed as ‘‘a conceptual stimulus of ideas and not as a strict statistical hypothesis that must be proven or disproven’’ (Childers et al. 2000).

Until recently, inorganic carbon had not been a major topic in the discussion of the outwelling hypothesis. However, the concentrations, temporal changes, and spatial variations of total dissolved inorganic carbon (DIC) and surface water $p\mathrm{CO_2}$ provide critical data for revealing how these systems function at the biogeochemical level (Gattuso et al. 1998; Cai et al. 2000). Not only do inorganic carbon data provide a key to assessing the metabolism of a coastal system (Smith and Hollibaugh 1993), they also have direct implications for global carbon cycling (e.g., Tsunogai et al. 1999; Frankignoulle and Borges 2001*a*). Recent data sets of inorganic carbon and surface water $p\mathrm{CO_2}$ in coastal systems have indicated that estuaries and in-shore systems are net heterotrophic and are potential significant sources of atmospheric CO_2 (Frankignoulle et al. 1996; Gattuso et al. 1998). Meanwhile, marsh-influenced estuaries have been identified as important sources of inorganic carbon to their adjacent coastal waters (Winter et al. 1996; Cai and Wang 1998; Cai et al. 1999, 2000; Raymond et al. 1997, 2000; Neubauer and Anderson 2003).

The metabolic state of a system represents the trophic balance between gross primary production (GPP) and total respiration (R) and is defined as net ecosystem production (NEP $=$ GPP $-$ R) (Smith and Hollibaugh 1993; Kemp et al. 1997; Smith and Hollibaugh 1997). Generally speaking, in a net autotrophic system (NEP > 0), the excess organic carbon (OC) synthesized by photosynthesis is exported or buried, and the concentrations of nutrients and inorganic carbon remain low. In a net heterotrophic system (NEP < 0), allochthonous organic matter is broken down and the system releases inorganic nutrients and CO_2. The central concept of NEP, therefore, reflects the balance between organic carbon production and decomposition, or the balance between organic carbon export and import for a particular system (i.e.,

---

[1] Present address: College of Marine Science, University South Florida, St. Petersburg Campus, 140 Seventh Avenue South, St. Petersburg, Florida 33701.

[2] Corresponding author (wcai@arches.uga.edu).

Acknowledgments

This study was funded by GCE-LTER program (NSF-OCE 99-82133). We thank the captains and crews of R/V *Blue Fin* and R/V *Savannah* for the support of the surveys. We have benefited greatly from many discussions with L. R. Pomeroy. Comments by two reviewers and the associate editor R. Hesslein improved the quality of this paper. Y. Wang and G. Han provided vital field and laboratory support. W.-J. Cai thanks George Davidson for English editing and support over the years. Z. A. Wang acknowledges the Dissertation Completion Assistantships provided by the Graduate School of the University of Georgia. He also thanks his Ph.D. committee members William Wiebe, Merryl Alber, James T. Hollibaugh, and Richard A. Jahnke for insightful suggestions.

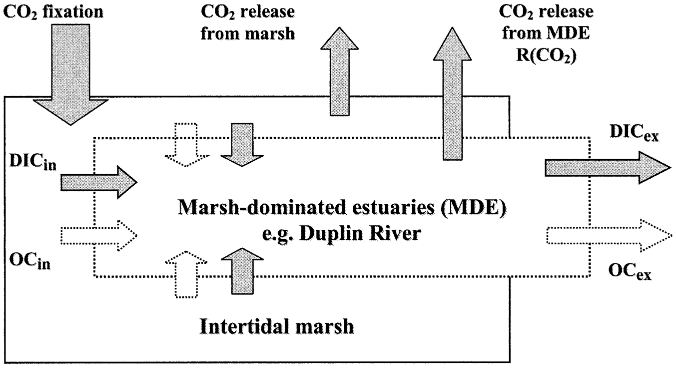

Fig. 1. A conceptual representation of apparent net heterotrophy (ANH) and inorganic carbon fluxes (gray arrows) for a marsh-dominated estuary (MDE). Organic carbon fluxes (white arrows) from previous findings (Wiegert et al. 1983; Chalmers et al. 1985; Hopkinson 1988) are also plotted. $R(CO_2)$, CO_2 release from MDE; OC_{ex} and DIC_{ex}, exports of organic and inorganic carbon from MDE; OC_{in} and DIC_{in}, inputs of organic and inorganic carbon from marshes into MDE; $ANH = DIC_{ex} + R(CO_2)$.

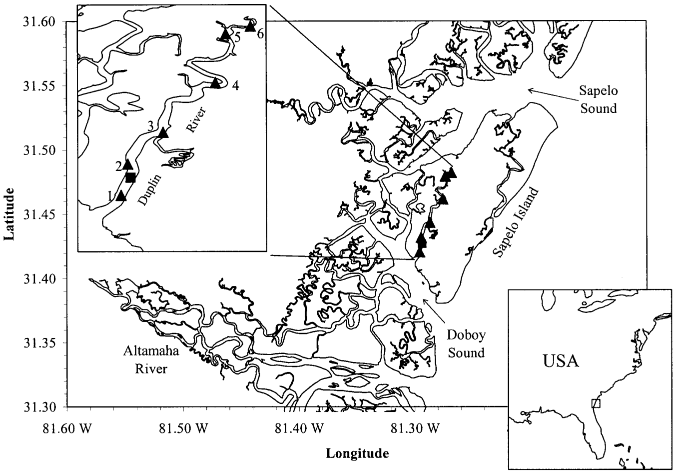

Fig. 2. Study area and sampling stations. The filled square represents the anchor station in the Duplin River. Six stations (triangles) along the Duplin River (inset), from the river mouth upstream, were Marsh Landing (1), Little Sapelo Island (2), Barn Creek (3), Lumber Landing (4), Hunt Camp (5), and Flume Dock (6). Three nearby areas within the GCE-LTER domain are also shown.

NEP = OC exports − OC imports). Note that in this discussion we assume that net inventory change within a system is negligible when compared to the export fluxes.

With respect to inorganic carbon, if a water system is heterotrophic, excess inorganic carbon released from respiration would be exported and/or lost as CO_2 to the atmosphere by air–water exchange. In addition to river input, a marsh-influenced riverine estuary may also receive substantial amounts of inorganic carbon from its adjacent marsh, while exporting inorganic carbon to coastal waters and degassing CO_2 to the atmosphere. Therefore, NEP = DIC import − (DIC export + CO_2 degassing). For marsh-influenced nonriverine estuaries, marsh effects with respect to inorganic carbon are often dominant due to limited freshwater input. Many Georgia coastal systems fall into this category. We call an estuary of this type a ‘‘marsh-dominated estuary’’ (MDE) in the context of this study. We also define the estuary in this study as the water area of the main channel not including the ambient marshes unless otherwise indicated in order to accommodate our dataset and to conform to tradition.

Since DIC imports from marshes to an estuary cannot be clearly defined, we use apparent net heterotrophy (ANH) to define the sum of the two inorganic carbon export terms, DIC export and CO_2 degassing from a marsh-dominated estuary (Fig. 1). The ANH simply represents the total inorganic carbon loss from such a system (Fig. 1), and it does not necessarily mean that the estuarine system is net heterotrophic. The ANH is used as an indicator of the export of inorganic carbon from the marsh in the later discussion. Raymond et al. (2000) argued that, after deducting riverine influence, the sum of these two inorganic carbon teams must be balanced by net heterotrophy in an estuary (not including adjacent marshes). This argument should be modified since the estuary also receives its inorganic carbon from the surrounding marsh and estuarine respiration only partially supports these two inorganic carbon sink teams in an MDE.

In this study, we investigate seasonal variations of the CO_2 system in the Duplin River, a marsh-dominated blind tidal river on Sapelo Island. It sets the stage to revisit the outwelling hypothesis from the viewpoint of inorganic carbon mass balance. We quantify DIC export and CO_2 degassing to examine seasonal changes of the total loss of inorganic carbon (or the ANH) from the system and its supporting mechanisms.

The hypothesis to be tested behind this quantification is that intertidal salt marshes are significant sources of inorganic carbon to the adjacent coastal water. Furthermore, we argue that inorganic carbon released from salt marshes also has significant influence on the CO_2 system in the adjacent continental shelf based on estimated marsh export fluxes of inorganic carbon in the Duplin River. Finally, a ‘‘marsh CO_2 pump’’ concept is proposed to characterize the seasonality of the export of inorganic carbon from marshes and discuss the role of marsh-dominated estuaries in transferring inorganic carbon from the atmosphere to the ocean.

Study site and methods

Study site—This study is part of the ongoing Georgia Coastal Ecosystems (GCE) Long Term Ecological Research (LTER) project. The Duplin River is located in the center of the GCE-LTER study area (Fig. 2). Sapelo Sound and Doboy Sound lie to its north and south, respectively. The Duplin River is a tidal slough at its entrance into Doboy Sound (Fig. 2). The use of the term river for sections of braided estuaries is unique to coastal South Carolina and Georgia. The Duplin River is therefore not a real river in the normal meaning of the word. A detailed site description can be found in Pomeroy and Wiegert (1981). Briefly, it is surrounded by intertidal salt marshes and is a marsh-dominated estuary. Its upper stream is the water that actually resides in the marshes at high tide or ‘‘marsh water’’ (Imberger et al. 1983).

The only freshwater sources at the headwaters are rainfall on the surrounding marshes and island groundwater runoff. During the high-flow seasons (winter and spring), freshwater from a regional large river, the Altamaha River, may occasionally enter the Duplin River via Doboy Sound, which connects to the Altamaha River through its upper stream and the Intercoastal Waterway. Tidal exchange is usually the primary driving force for interactions between estuarine water and salt marshes in the Duplin River except during storm events and freshwater intrusion.

Monthly sampling and anchor monitoring—The samples for total dissolved inorganic carbon (DIC), total alkalinity (TA), and pH were collected monthly (September 2000–April 2002) at six fixed stations using a small boat (Fig. 2). From the mouth heading upstream, they were Marsh Landing, Little Sapelo Island, Barn Creek, Lumber Landing, Hunt Camp, and Flume Dock. There was no sampling in October 2000. During the sampling day of each month, surface water at the six stations was collected twice for consecutive high and low tides. Temperature and salinity were recorded in situ using a conductivity-temperature-depth (CTD) sensor (Seabird). DIC, TA, and pH samples were taken in 125-ml acid-cleaned glass bottles, and 10 μl of saturated $HgCl_2$ solution was added for preservation. Surface water pCO$_2$ was calculated from temperature, salinity, DIC, and pH using carbonate equilibrium constants (K_0, Weiss 1974; K_1 and K_2, Cai and Wang 1998).

To investigate the effects of tidal exchange on the water column CO_2 system over tidal cycles, continuous monitoring of surface water pCO$_2$ was performed at an anchor station inside the Duplin River (Fig. 2) on 17 September 2000, 20 March, 26 June, 11–13 October, and 27–29 November 2001. Discrete surface water samples for DIC and TA were also collected through an inlet of the on-board pumping system during each anchoring. The anchor monitoring was part of the seasonal GCE-LTER surveys performed on board of R/V *Bluefin* and R/V *Savannah* (Wang 2003). Each anchoring lasted 5 to 36 h depending on the survey schedule, and water sampling was conducted at 1- or 3-h intervals.

Continuous monitoring—During the anchor monitoring, surface water was continuously pumped on board from the bottom of the research vessel (2.6 m below surface) and was measured for pCO$_2$, temperature, and salinity. Temperature and salinity were monitored by a flow-through Seabird CTD. pCO$_2$ was measured by a ‘‘combined laminate-flow and shower-head equilibrator plus an infrared analyzer (Li-Cor 6252)’’ system. The design and configuration of this system followed those presented in the literature (Feely et al. 1998; Körtzinger et al. 2000; Frankignoulle and Borges 2001*b*). The pCO$_2$ system was calibrated on board every 4 h by flowing known gas standards (BOC Gasses) through the system. These on-board used standards were calibrated against a gas standard from the National Institute of Standards and Technology (NIST) using a Li-Cor 6252 CO_2 analyzer. Through laboratory verification, the precision of the pCO$_2$ system was better than 1 μatm pCO$_2$. All pCO$_2$ measurements were corrected for water vapor pressure and temperature, and final results reflected pCO$_2$ at 1 atmospheric pressure with 100% saturation of water vapor and in situ temperature. All underway data were binned at 1-min intervals for presentation.

Sample analysis—DIC was measured with an automated DIC analyzer. The system was calibrated using certified reference material (CRM) from A. G. Dickson of Scripps Institution of Oceanography. It used small-volume (0.1–1.0 ml) samples, and each measurement cycle was less than 5 min. The system consisted of a nondispersive infrared CO_2 analyzer (Li-Cor 6262), a precision digital syringe pump, a gas flow controller, and a CO_2 stripping reactor. The syringe pump was used to pump the sample (normally 0.5 ml) and acid (1 ml of 10% H_3PO_4) into the reactor after all of the solution in the previous analysis was purged. The CO_2 extraction system consisted of a gas flow line, the reactor, and a gas-drying unit. The body of the reactor was wrapped with an electronic cooling system, which was set below $\sim$3°C. Thus, a low water vapor pressure was maintained in the reactor. The gas flow was further dried through a $Mg(ClO_4)_2$ plug (about 10 ml). The Li-Cor CO_2 detector was used to measure CO_2 gas concentration. The detector had a baseline noise of $<$0.3 μatm. Finally, DIC was calculated by integrating the area under the CO_2 curve over time ($<$2 min). The entire procedure was controlled by a computer. Based on replicate analysis, the precision of the DIC analyzer was 0.10–0.15% of a DIC value or of the total area under the integration curve.

TA was determined in a 40-ml sample by Gran titration (Gran 1952) to an endpoint pH of 3.2 using HCl solution. The titrations were carried out by an automated device using a Kloehn digital syringe and drive modules (Kloehn). The HCl standard solution was calibrated with CRM. The precision of the titration was 0.1–0.15%. The results are reported in μmol kg^{-1} instead of μeq kg^{-1}, which one may read as μmol HCl used for titration of 1 kg of sample solution. Further details of the DIC analyzer and the TA titrator are available from the corresponding author.

pH was measured at a constant temperature (25°C) using a Ross glass pH electrode (Orion Research). The calibration was conducted using standard buffer solutions (pH $=$ 4, 7, 10) with NIST scale. The relative accuracy was $\pm$0.01 pH unit.

Respiratory rates—Water column respiratory rates were determined by on-board dark incubations with surface water at the mouth of the Duplin River during each GCE-LTER survey. Surface water was collected in a 50-liter carboy and mixed well. The water was subsequently allowed to overflow into six 1-liter opaque glass bottles. In three of them, 500 μl of saturated $HgCl_2$ solution was added for the purpose of stopping biological activity and documenting the initial conditions of incubation. The other three bottles served to measure changes during the incubation. Each bottle was wrapped with a black plastic bag and placed inside an opaque ice chest through which running surface water flowed. The incubation lasted 24 to 36 h. DIC samples were collected for laboratory analysis. The respiratory rates were calculated from changes in DIC concentrations over the time of incubation and represented time-averaged values (Table 1).

Table 1. Water-column respiratory rates measured at the mouth of the Duplin River. All results were converted from the unit of mmol C m^{-3} d^{-1} to mmol C m^{-2} d^{-1} by multiplying the water depth of 5 m at the station.

	Mar 2001	Jun 2001	Oct 2001	Nov 2001
mmol C m^{-2} d^{-1}	20.3±6.8	89.3±19.9	48.1±17.3	87.1±17.1

These results are used as supplementary data in the discussion.

Air–water CO_2 flux—The CO_2 fluxes across the air–water interface were calculated by the following one-dimensional stagnant-film model:

$$CO_2 \text{ flux} = k\beta\,(pCO_{2w} - pCO_{2a}) \quad (1)$$

where k is the gas transfer velocity; β (Bunsen coefficient) is the solubility of CO_2 (Weiss 1974); pCO_{2w} and pCO_{2a} represent the partial pressure of CO_2 in surface water and overlying air, respectively. The main uncertainty in this calculation results from the estimation of gas transfer velocity (k), which is empirically derived from wind speed. For the sake of comparison, two sets of equations were used to calculate k. One was taken from Wanninkhof (1992) (hereafter referred to as W); another was from Raymond et al. (2000) (hereafter referred to as R). The W method has been applied mostly to open-ocean conditions, while the R method was derived from estuarine tracer experiments. It is believed that morphology and physical conditions in estuaries are different from those in the open ocean (Frankignoulle et al. 1998; Raymond et al. 2000), so the traditional relationship between wind speed and gas transfer velocity applied in open-ocean studies (e.g., W method) may not be suitable for calculation of CO_2 fluxes in estuaries. We therefore used both relationships to examine their potential differences.

Results

Monthly data in the Duplin River—Monthly data in the Duplin River reflected a complete annual variation of the CO_2 system in a marsh-dominated estuary (Fig. 3). All stations showed a similar variation pattern for each measured parameter. Generally, DIC and TA at a fixed station covaried with salinity with an annual minimum value in March and a maximum in December during the sampling period (Fig. 3). Seasonal changes for DIC and TA were as large as over 1000 μmol kg^{-1}. The large dip of DIC, TA, and salinity in March 2001 is believed to be a result from intrusion of the fresher Altamaha River water (via Doboy Sound) bearing low inorganic carbon content and alkalinity (Wang 2003). From spring to fall, DIC and TA continued to rise and reached around 2,600 μmol kg^{-1} at all stations. Tidal low water tended to have higher inorganic carbon and alkalinity than tidal high water. This difference was most noticeable from September to December at the downstream stations (Fig. 3). Although our sampling in the Duplin River did not necessarily capture the same water mass at a fixed station during two consecutive tidal stages for each sampling event, such a difference indicates release and export of inorganic carbon and alkalinity from marshes in summer and fall.

Seasonal change of surface water pCO_2 was over 3,000 μatm (Fig. 3). The lowest pCO_2 occurred in January and February, which coincided with the annual lowest water temperature. Surface water pCO_2 continued to rise from February to June along with temperature. During summer and fall, its value was consistently high at 2,000–3,000 μatm level for all stations. A large difference between high and low tide at a fixed station, especially downstream stations, was pronounced for pCO_2 from June to December (Fig. 3). The pCO_2 values at low-tide waters were sometimes more than 2,000 μatm higher than the high-tide values, indicating that the marsh is a strong inorganic carbon source in summer and fall. Oversaturation of surface water pCO_2 with respect to the atmospheric level (measured at 380–390 μatm in these areas) during the entire sampling period (Fig. 3) suggested that the surface water of the Duplin River degases CO_2 to the atmosphere year round.

Annual variation of pCO_2 was negatively correlated to pH for all stations in the Duplin River (Fig. 3). Regression analysis showed that their relationship was strong but nonlinear. In general, high pH values were observed in spring and winter, while low values occurred in summer and fall (Fig. 3). Seasonal differences were as large as 0.5 pH unit. Low-tide waters usually had lower pH values than high-tide waters, which was consistent with higher pCO_2 in low-tide water. This pattern was also most clear at downstream stations (Fig. 3).

Spatially, tidal averages of DIC values generally increased upstream from Marsh Landing (0.7 km from the mouth) to Flume Dock (12 km from the mouth) (Fig. 4). A similar pattern was observed for TA, but with exceptions (e.g., January and February, Fig. 4). Furthermore, this longitudinal gradient experienced a seasonal progression (Fig. 4). From January to March, DIC and TA in the water were low, and their longitudinal differences were small, except for March of 2001, when freshwater intrusion from the Altamaha River into the lower and middle sections of the Duplin might cause the observed large DIC and TA gradients in the upper stream (Wang 2003). In early summer, DIC and TA and their gradients were elevated at all stations. From July to December, the longitudinal gradients of DIC and TA were generally strong with a difference of as large as over 200 μmol kg^{-1} between Marsh Landing and Flume Dock. Similarly, surface water pCO_2 increased from Marsh Landing to Flume Dock during each sampling event, and the corresponding gradients were especially steep in summer (Fig. 4). Since the water in the upper Duplin River has more contact with marshes, spatial distributions presented here again indicate that the salt marshes are a source of inorganic carbon and alkalinity most of the year.

Anchor monitoring in the Duplin River—Effects of tidal cycles on the CO_2 system in the Duplin River also showed seasonality and were consistent with the monthly monitoring data (Fig. 5). In March, low-tide waters contained less DIC and TA compared to high-tide waters. Meanwhile, surface water pCO_2 was as low as 500 μatm at high tide and 800 μatm at low tide (Fig. 5). The maximum pCO_2 of the low-

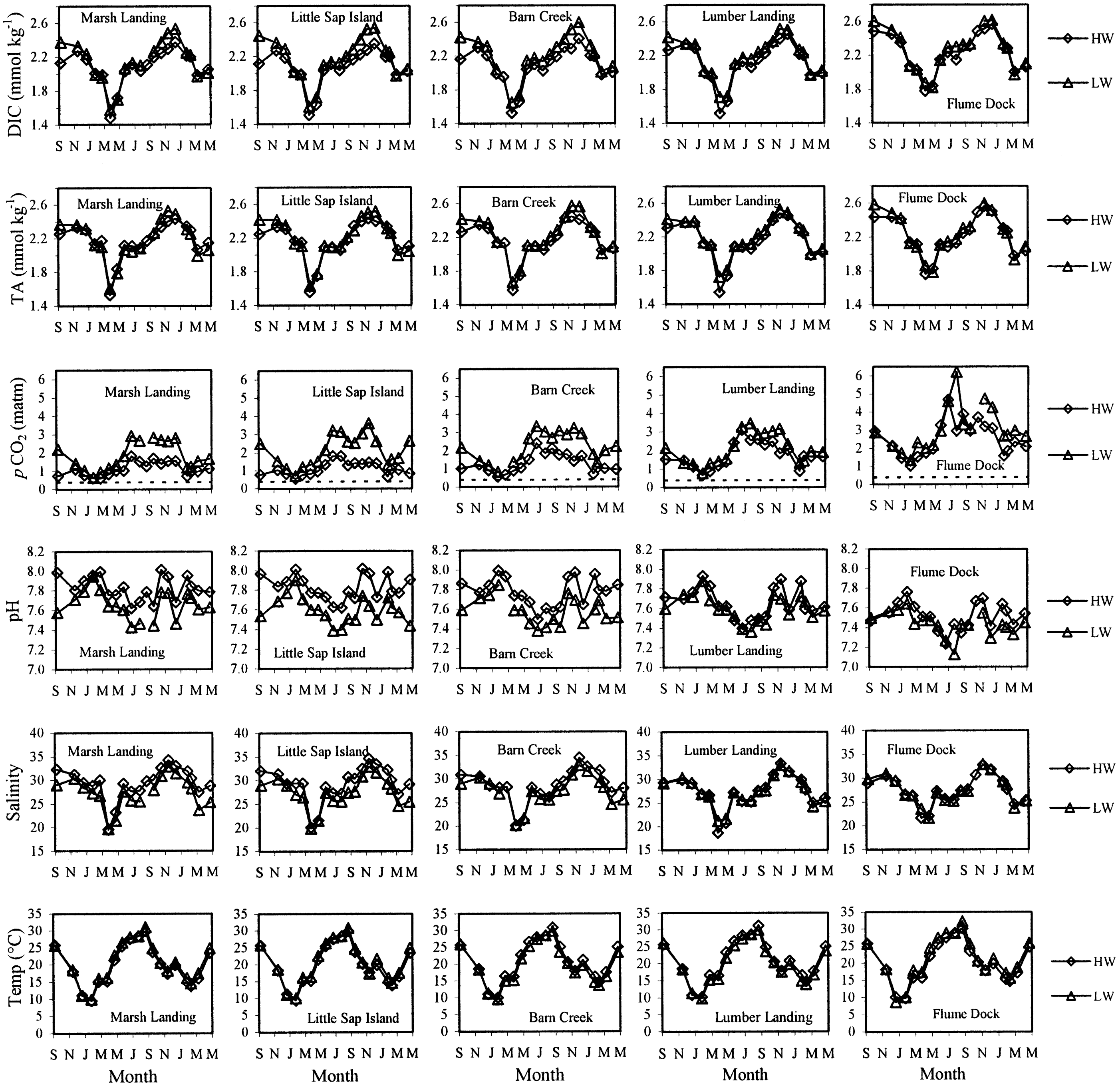

Fig. 3. Annual variations of surface water DIC, TA, pH, pCO$_2$ (calculated from DIC and pH data), salinity, and temperature at five sampling stations (Marsh Landing, Little Sapelo Island, Barn Creek, Lumber Landing, and Flume Dock) in the Duplin River. The data from Hunt Camp, which is close to Flume Dock, is not shown. HW and LW in the plots refer to high-water and low-water sampling, respectively. The dashed lines in pCO$_2$ plots represent the average atmospheric CO$_2$ level (385 μatm). While μmol or μatm are used throughout this paper, mmol or matm are used in Fig. 3 due to space limitation.

tide water in June increased to about 2,500 μatm, while the high-water minimum was about 700 μatm (Fig. 5). Variations of DIC and TA during one tidal cycle were small in this early summer month, with a difference of only 100 μmol kg^{-1} between low- and high-tide waters (Fig. 5). pCO$_2$ and its magnitude of variation during a tidal cycle were similar in September and June (Fig. 5). However, DIC and TA values at low water in September were over 200 μmol kg^{-1} higher than those at high water (Fig. 5). This pattern continued in October and November for DIC and TA, while surface water pCO$_2$ decreased dramatically (Fig. 5). In late November, surface water pCO$_2$ dropped to the March level (Fig. 5).

Anchor monitoring in March, October, and November (Fig. 5) occurred over the daily light and dark conditions.

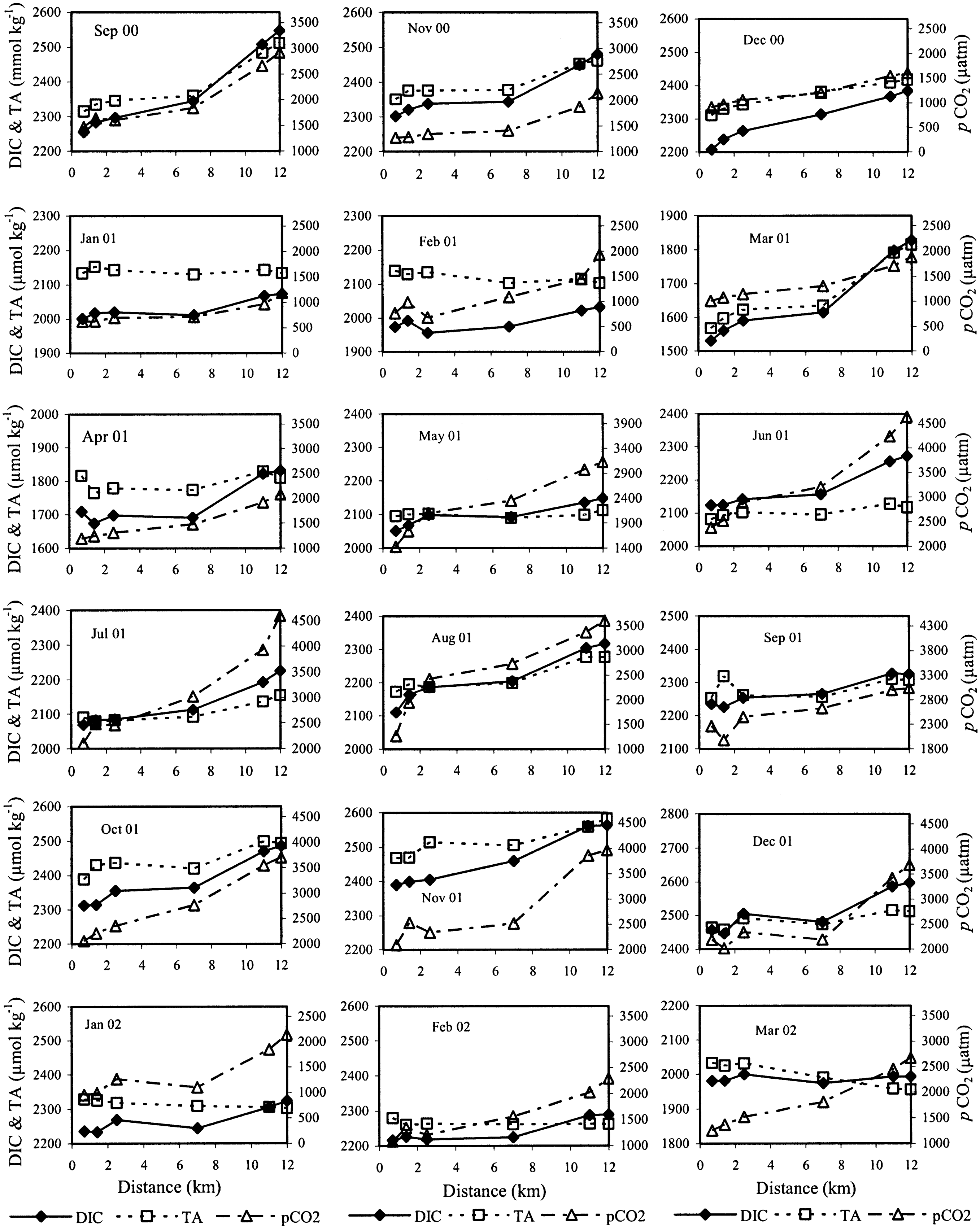

Fig. 4. Spatial distributions of DIC, TA, and pCO$_2$ from the monthly sampling events in the Duplin River.

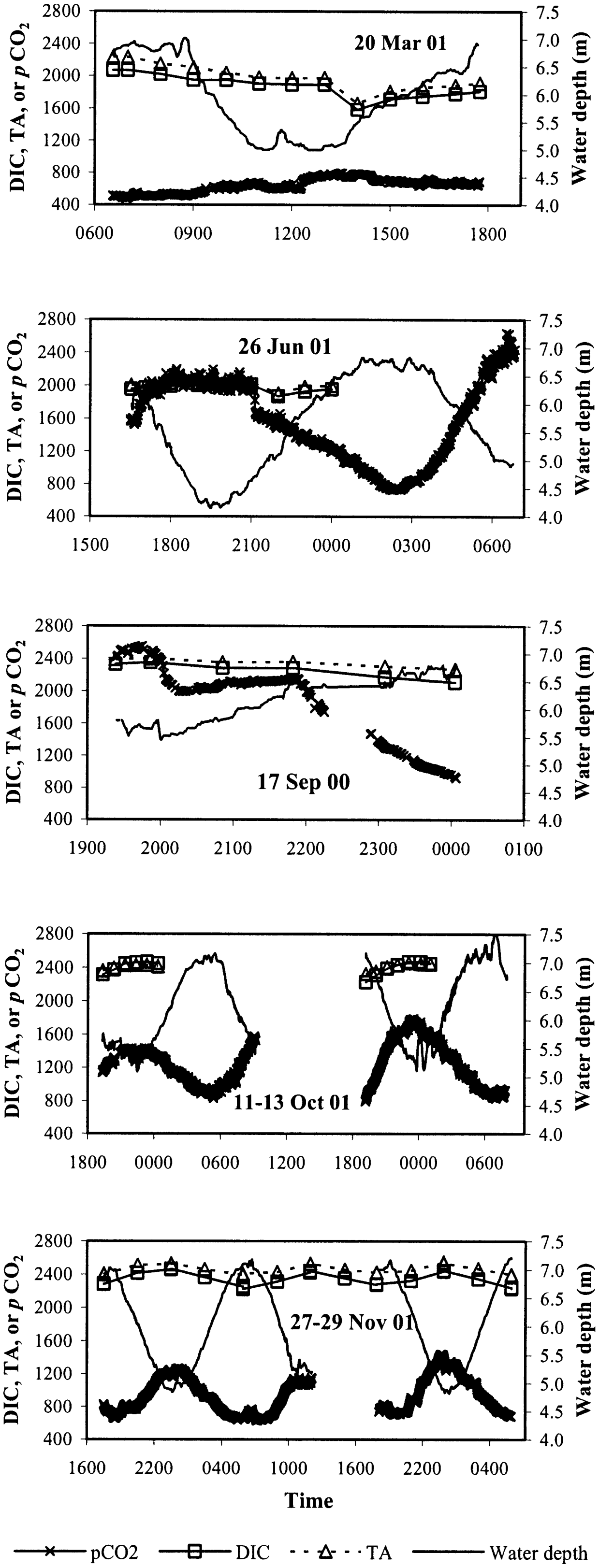

Fig. 5. Time series plots of surface water pCO_2, DIC, TA, and water depth at the Anchor Station in the Duplin River during the five GCE-LTER surveys. DIC and TA are in units of μmol kg^{-1}, and pCO_2 is in μatm.

However, the variability of inorganic carbon parameters was mostly related to tidal periods. Diurnal changes, if any, account for an insignificant portion of the total changes as indicated by the small difference of pCO_2, DIC, and TA between the light and dark conditions at similar tidal phases (Fig. 5). Owing to limited freshwater influence, tidal exchange with marshes plays a crucial role in modifying the CO_2 system in the water of the Duplin River. On the other hand, DIC, TA, and pCO_2 values were mostly repeatable from one tidal cycle to the next in November, when anchor monitoring covered 2–3 tidal cycles. This implies that the processes that release inorganic carbon in marshes have an overall turnover time much longer than one tidal cycle, as was suggested for silicate in the Duplin River (Imberger et al. 1983). It also implies that although salt marshes in the Duplin River release inorganic carbon into the tidal water, tidal oscillation is probably not an efficient way to export it over a short time scale. Instead, longitudinal eddy diffusion usually provides a major means to move marsh-produced material out of the Duplin River, except during storm events (Imberger et al. 1983; Chalmers et al. 1985). Therefore, the longitudinal gradients of DIC and TA observed in Fig. 4 can be translated into actual export fluxes through an eddy diffusion equation.

Estimates of CO_2 degassing, DIC export, and apparent net heterotrophy—With basic information on geomorphology, hydrology, and meteorology of the Duplin River, we can quantify air–water CO_2 fluxes and DIC exports on a monthly basis. This quantification would provide a detailed picture of seasonal variations of DIC export and air–water CO_2 exchange in the Duplin River and allow us to assess annual variability of the marsh as an inorganic carbon source.

To calculate an area-weighted mean CO_2 flux and to determine its spatial pattern, the 12-km long Duplin River was divided into five segments. Each segment was bounded by two consecutive sampling stations (Fig. 2). The mean pCO_2 of a segment was calculated by averaging high-water and low-water pCO_2 at a station and then taking the mean of two adjacent stations. These segment pCO_2 means were then used to estimate the CO_2 flux of each segment. The segment CO_2 fluxes were area weighted to obtain a mean CO_2 flux for the entire river (Table 2).

CO_2 fluxes calculated from the W method were lower than those from the R method, except for one case when the averaged wind speed was over 4 m s^{-1} (Table 2). The difference between the two methods was 48% on average for area-weighted mean CO_2 fluxes at wind speeds of less than 3.5 m s^{-1}. For wind speeds between 3.5 and 4.0 m s^{-1}, the difference was only 11%. Higher CO_2 fluxes from the R method might be expected because of inherently greater turbulence in estuarine environments (Frankignoulle et al. 1998; Cai et al. 1999; Raymond et al. 2000). However, more independent studies are necessary to refine CO_2 flux calculations in estuarine waters. The difference in the CO_2 fluxes from two methods in this study was less than 50%, which is similar to that in offshore studies (e.g., Wanninkhof 1992; DeGrandpre et al. 2002).

The net export flux of DIC from Marsh Landing in the

Table 2. CO_2 fluxes in the Duplin River. Numbers are in mmol m^{-2} d^{-1} unless otherwise indicated. The results calculated from both Wanninkhof (1992) (W) and Raymond et al. (2000) (R) parameterizations are listed. The annual flux was calculated by integrating daily flux from January 2001 to December 2001. Positive values indicate fluxes are from water to the atmosphere. Segment 1, Marsh Landing to Little Sap Island; Segment 2, Little Sap Island to Barn Creek; Segment 3, Barn Creek to Lumber Landing; Segment 4, Lumber Landing to Hunt Camp; Segment 5, Hunt Camp to Flume Dock. Area-weighted average CO_2 fluxes were calculated by multiplying each segment's flux by its surface area, summing the five segment fluxes, and dividing by the total surface area of five segments. Surface areas (all in 10^5 m^2) are 0.9, 1.3, 4.9, 3.0, 0.5 for segments 1–5, respectively, which were estimated based on the distance between two consecutive stations (Imberger et al. 1983) and the river width measured from a 1 : 80,000 scale map.

Date	Average daily wind speed ($m\ s^{-1}$)	Segment 1		Segment 2		Segment 3		Segment 4		Segment 5		Area-weighted average	
		W flux	R flux	W flux	R flux	W flux	R flux	W flux	R flux	W flux	R flux	W flux	R flux
Sep 2000	3.95	45.4	46.7	48.0	49.4	51.9	53.5	72.5	74.6	93.5	96.2	58.9	60.6
Nov 2000	2.79	17.6	30.9	18.3	32.2	19.6	34.4	24.8	43.5	32.0	56.2	21.4	37.5
Dec 2000	3.55	18.3	22.2	20.8	25.3	24.7	30.1	32.9	40.0	39.6	48.2	26.8	32.6
Jan 2001	3.04	6.1	9.4	7.0	10.8	8.1	12.5	11.4	17.5	17.1	26.5	9.2	14.2
Feb 2001	3.11	12.5	18.6	11.4	16.9	12.8	19.0	22.4	33.3	33.0	49.1	16.4	24.3
Mar 2001	4.26	32.1	29.4	35.3	32.4	41.0	37.6	54.2	49.8	67.9	62.3	44.7	41.0
Apr 2001	3.75	30.5	34.1	32.6	36.4	37.0	41.4	47.8	53.4	58.7	65.6	40.1	44.8
May 2001	3.95	46.9	48.3	60.2	62.0	72.4	74.5	89.5	92.1	104.7	107.7	75.3	77.5
Jun 2001	3.61	67.8	80.3	76.2	90.2	87.7	103.8	110.0	130.3	133.8	158.4	93.4	110.6
Jul 2001	3.62	62.9	74.3	68.9	81.4	78.1	92.2	102.6	121.2	128.6	151.9	85.3	100.8
Aug 2001	3.50	37.7	46.9	55.9	69.5	68.4	85.1	83.8	104.2	97.3	121.0	70.2	87.3
Sep 2001	3.38	49.5	64.9	52.1	68.4	61.6	80.8	69.6	91.3	75.6	99.1	62.5	81.9
Oct 2001	3.86	65.1	69.6	70.9	75.7	81.3	86.9	103.5	110.6	121.1	129.4	87.1	93.0
Nov 2001	3.47	58.0	73.1	61.6	77.7	61.6	77.6	84.5	106.5	106.2	133.9	70.1	88.4
Dec 2001	2.94	36.8	59.8	38.6	62.7	40.6	66.0	52.1	84.7	68.2	110.9	44.7	72.7
Jan 2002	2.86	12.4	21.0	15.6	26.4	16.9	28.6	22.9	38.8	33.8	57.2	18.9	32.1
Feb 2002	3.01	19.7	30.8	21.2	33.1	23.8	37.2	33.3	52.1	41.8	65.4	26.8	41.9
Mar 2002	3.60	31.5	37.4	35.8	42.6	43.4	51.6	59.1	70.3	73.7	87.6	47.5	56.5
Apr 2002	3.40	34.6	44.9	37.7	49.0	38.6	50.1	51.8	67.3	60.4	78.5	43.0	55.9
g C m^{-2} yr^{-1}												256.2	306.4
Annual mmol m^{-2} d^{-1}												58.5	70.0

Duplin River can be evaluated using a diffusion-type equation based on the finding that exchange between the upper and lower water masses mostly takes place by eddy diffusion (Imberger et al. 1983):

$$Q = \varepsilon\langle A\rangle \frac{C_i - C_{ML}}{L} \qquad (2)$$

where Q represents the flux; ε is the effective longitudinal diffusion coefficient; $\langle A\rangle$ is the cross-sectional area at Marsh Landing; C_i and C_{ML} are the tidal average of the mean DIC at station i and Marsh Landing, respectively; L is the distance along the river from Marsh Landing to station i; and $(C_i - C_{ML})/L$ represents the concentration gradient. The same equation has also been used in the estimation of organic carbon exports from the Duplin River (Wiegert et al. 1981; Chalmers et al. 1985). Imberger et al. (1983) derived a mean ε of 38 m^2 s^{-1} based on mass-balance calculation of the longitudinal salt flux along the Duplin River after a rain event. $\langle A\rangle$ was estimated to be 654 m^2 at Marsh Landing. The distance L was obtained from Imberger et al. (1983). C_{ML} and C_i were calculated by averaging high- and low-water DIC concentrations at individual stations for each sampling event. Daily export flux of DIC (mmol d^{-1}) from the Duplin River was calculated using the mean DIC gradient by averaging the individual gradients between Marsh Landing and five upstream stations. The resulting daily DIC export fluxes (mmol d^{-1}) were divided by the total surface water area from Marsh Landing to Flume Dock to convert the values to areal export fluxes (mmol m^{-2} d^{-1}) (Fig. 6a). The uncertainty associated with averaging DIC gradients was 20–30%. Ignorance of variation of the diffusion coefficient (e.g., due to storm events and spring–neap tide cycles) may also introduce uncertainty. The uncertainty from DIC sample analysis is negligible. Finally, apparent net heterotrophy (ANH) in the Duplin River was calculated by adding areal DIC export and CO_2 degassing (Fig. 6a).

The upper two sections between Lumber Landing and Flume Dock in the Duplin River (Fig. 2) contain mostly marsh water (Imberger et al. 1983; Chalmers et al. 1985). For comparison, the entire procedure presented above was also used to estimate DIC export and CO_2 degassing from these two sections (Fig. 6b).

Errors associated with an infrequent sampling scheme—An infrequent sampling scheme could potentially lead to a gross misunderstanding of system behavior as illustrated by an example from a coastal embayment where the O_2 level varied greatly over a daily cycle (Taylor and Howes 1994). This particular system was dominated by the production and destruction of plankton. The issue is different in a salt-marsh system, where production is accomplished mostly by standing plants taking CO_2 from and releasing O_2 to the air. The

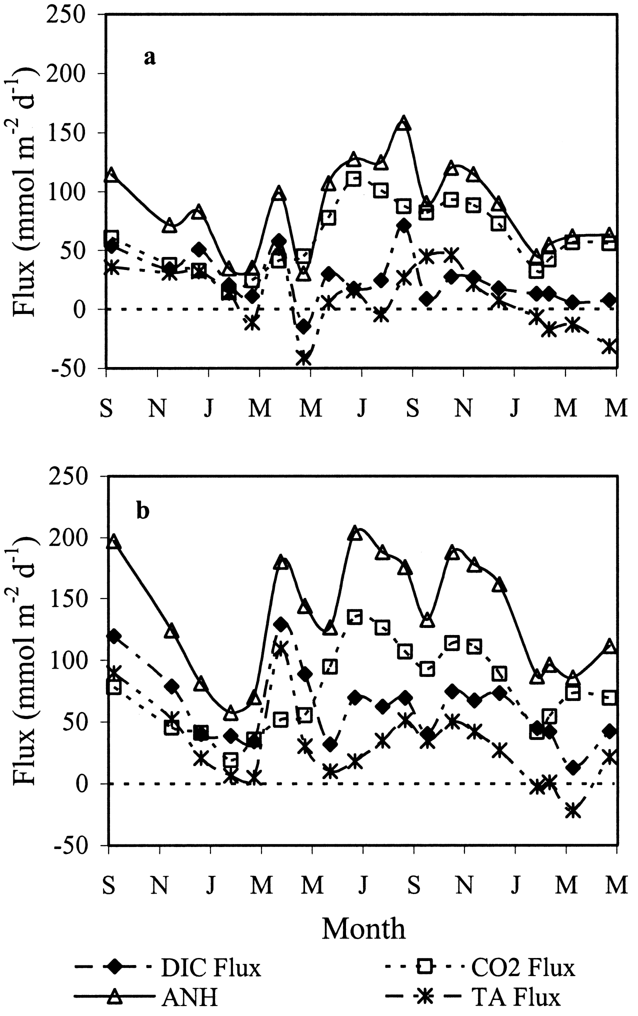

Fig. 6. Areal fluxes of DIC export, air–water CO_2 exchange, TA export, and the apparent net heterotrophy (a) relative to Marsh Landing and (b) relative to Lumber Landing in the Duplin River. Only CO_2 fluxes calculated from the method of Raymond et al. (2000) were displayed.

water column is dominated by the decomposition of dead organic mater and is balanced by gas exchange with the atmosphere; both processes have small daily variation. However, diurnal and tidal variations do occur over the marsh (Cai et al. 1999). Such signals are smaller in the main creek channel where we did our measurements.

In our work, we use the mean of two consecutive high- and low-water samples to represent the tidal average for the flux calculation. Variations in the CO_2 system due to tidal cycles, different water masses, and diurnal changes may introduce uncertainty in flux calculation. Based on the data from the anchor station that covered both tidal and diurnal cycles (Fig. 5), the variation of DIC between different cycles was about 20 μmol kg^{-1} (standard deviation between similar tidal phases). This was only 15% of the average DIC gradient between Marsh Landing and Flume Dock during the study period. Such variation may be significant in January and February when the DIC gradients were small in the Duplin River (Fig. 4). As for pCO_2, the variation from different cycles was only 50 μatm (Fig. 5), which was trivial when compared to the large air–water CO_2 gradients in the Duplin River at any time (Fig. 3). In terms of total of DIC and CO_2 fluxes (ANH), the uncertainty is quite small due to the infrequent sampling scheme.

Discussion

Seasonal variation of the apparent net heterotrophy—The ANH estimated for the entire Duplin River (Fig. 6a) and the upper two sections (Fig. 6b) showed a similar seasonal pattern with the maximum rate occurring in later summer and fall and the minimum in spring. Except in late winter and spring when surface water pCO_2 was below or near 1,000 μatm (Fig. 3), CO_2 degassing accounted for the major portion of the ANH and followed the seasonal pattern of the ANH closely. A sudden jump of the ANH in March 2001 (Fig. 6) corresponded to the large dips of DIC for all sampling stations (Fig. 3). As noted earlier, advection of freshwater with low DIC value from the Altamaha River via Doboy Sound may be responsible for this anomaly. The estimate of DIC export in this case may be uncertain because we based our calculation on the diffusion-type equation and assumed the net advection was negligible (Imberger et al. 1983). No sudden jump of DIC export occurred in spring 2002, and its variation was more gradual (Fig. 6).

Integrating monthly results from Table 2, the annual CO_2 degassing in the Duplin River (January 2001–December 2001) was 306 g C m^{-2} yr^{-1} (R method) or 256 g C m^{-2} yr^{-1} (W method). Meanwhile, the Duplin River discharged DIC of 109 g C m^{-2} yr^{-1} to Doboy Sound. The annual ANH was then 416 or 356 g C m^{-2} yr^{-1}, of which CO_2 degassing accounted for ca. 70%. Such a total loss of inorganic carbon (ANH) from the Duplin River was about four times the value estimated for the York estuary, Chesapeake Bay (Raymond et al. 2000). Both, however, followed a similar seasonal pattern. On the other hand, the annual export of DIC in the Duplin River is only one-tenth of the estimate in the Swartkops estuary, South Africa (1083 g C m^{-2} yr^{-1}; Winter et al. 1996). Similar to the Duplin River, the Swartkops estuary is also a marsh-dominated nonriverine tidal river, while the York estuary receives inputs from both river and marsh.

If the ANH in the Duplin River is mainly associated with marsh processes, and estuarine processes are of secondary importance, then annual variation of ANH (Fig. 6) generally reflects the annual variation of inorganic carbon release from marsh. Next we discuss the marsh's role in maintaining the ANH of the Duplin River.

Controls on the apparent net heterotrophy—Cai et al. (1999) have shown that respiration rates in waters of Georgia's riverine estuaries alone are insufficient to support the O_2 consumption and CO_2 degassing that are observed; the difference must be balanced by respiration in the water over intertidal marshes and in marsh sediment. Cai et al. (2000) have further demonstrated that Georgia's intertidal marsh is a source of inorganic carbon based on the estimates of DIC flux and CO_2 degassing in the Satilla estuary. Recent studies in several other estuaries all conclude that intertidal marshes adjacent to estuaries are sources of inorganic carbon (Winter et al. 1996; Raymond et al. 1997, 2000; Neubauer and Anderson 2003). In this study, we argue that the export of inorganic carbon from marshes is a main source supporting CO_2 degassing and the DIC export (or ANH) in a marsh-dominated estuary (Fig. 6).

Further discussion is needed to conclude that much of the ANH in the Duplin River is indeed the result of marsh processes. There are three tidal excursions over the length of the Duplin River (Ragotzkie and Bryson 1955; Imberger et al. 1983). A water mass from the upper Duplin River probably never reaches Doboy Sound advectively. However, salt and other materials can be transported along the river by continuous eddy diffusion. At the headwaters of the Duplin River, Imberger et al. (1983) defined a Lagrangian control volume, which approximately corresponds to the volume between Lumber Landing and Flume Dock (Fig. 2). The water in this control volume is the actual marsh water, since it is contained within the marsh during a typical high tide. Therefore, changes in the inorganic carbon signal in this volume reflect the net results of marsh processing. Meanwhile, the areal ratio of the marsh to the open water in the Duplin River is approximately 5:1 (Ragotzkie and Bryson 1955), and there are side creeks all the way down the river nearly to Doboy Sound. Therefore, we may argue that a strong marsh influence exists in most parts of the Duplin River, but the area least influenced is near the mouth. Indeed, the CO_2 fluxes show a gradient that decreased from the upstream section between Lumber Landing and Flume Dock to the lowest section near Marsh Landing (Table 2) except in February 2001. Such a gradient was largest in late summer and fall, and lowest in spring (Table 2). Moreover, the water at Flume Dock and Lumber Landing had higher DIC concentrations than the rest of the downstream stations during most times of the year (Fig. 4). DIC export from the upper two sections (Fig. 6b) was larger than that from Marsh Landing year round (Fig. 6a). Therefore, the ANH in the Duplin River must be primarily supported by marsh processes as a result of interaction between river water and the marsh.

Direct measurements of respiratory rates in marsh and estuarine waters provide evidence that inorganic carbon released from estuarine respiration alone cannot sufficiently support observed DIC export and CO_2 degassing in the Duplin River. The estuarine respiratory rates measured in spring, summer, and fall at the mouth of the Duplin River varied from 20 to 89 mmol C m^{-2} d^{-1} (Table 1). These rates were significantly less than the corresponding ANH (99–158 mmol C m^{-2} d^{-1}) during the same period. In contrast, the total respiratory rates in the marsh (marsh sediment + overlying water) were 82–183 mmol C m^{-2} d^{-1} (Pomeroy et al. 1972; Cai et al. 1999), which covered the range of the estimated ANH. Although the current inorganic carbon data did not allow us to separate the contribution of ANH from that of the intertidal marsh and from estuarine respiration, the available evidence leads us to conclude that a major portion of the ANH can be attributed to marsh processes. Therefore, temporal variations of the ANH in the Duplin River (Fig. 6) reflect the seasonal pattern of marsh respiration and water–marsh interaction with a high rate of inorganic carbon release from marsh in later summer and fall and a low rate in winter and spring. It is also concluded that marsh respiration plays an essential role in controlling the ANH in river water. Finally, in addition to a simple temperature effect, higher water column respiration rates during summer and fall as compared to springtime (Table 1) may reflect the fact that marshes export more labile organic carbon during summer and fall.

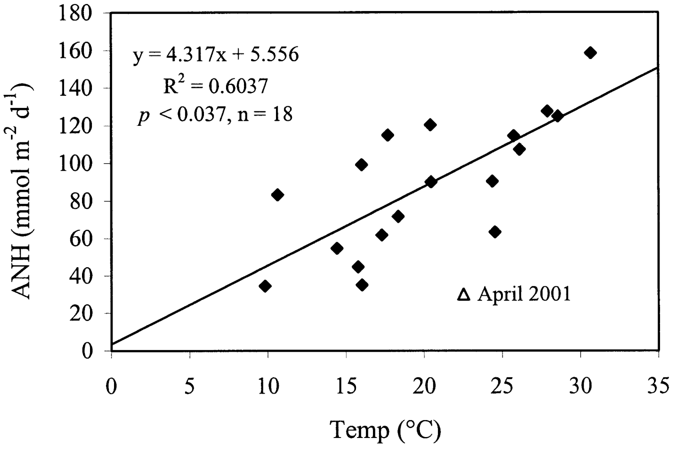

Fig. 7. Temperature dependence of the apparent net heterotrophy (ANH) in the Duplin River. Only the ANH relative to Marsh Landing (Fig. 6a) was used. The solid line represents the linear best fit of the data points with $R^2 = 0.6037$, $p < 0.037$, $n = 18$. The data from April 2001 were not included in the regression.

A significant positive relationship existed between the average temperature and the ANH in the Duplin River (Fig. 7). A major portion of the ANH consists of CO_2 degassing (Fig. 6), which is, if other conditions are kept constant, positively associated with temperature due to the thermodynamic nature of the CO_2 system. However, to sustain the higher CO_2 flux, rate of CO_2 generation must also be higher. Therefore, we suggest that temperature is probably a major factor mediating the respiratory release of inorganic carbon from the marshes. The temperature dependency of respiratory rates had been found to be significant in the marshes (Dame 1989) and in the five Georgia riverine estuaries (Pomeroy et al. 2000).

In order to examine the TA signal in the context of inorganic carbon export from the Duplin River and the marshes, areal export of TA was also estimated by using the same calculation as for DIC (Fig. 6). TA export generally matched seasonal variation of DIC export for most of the year with some exceptions in summer and fall (Fig. 6).

Aerobic respiration and its reverse process, photosynthesis, have significantly less influence on TA change than on O_2 and DIC changes because the stoichiometry of these reactions is $106C:17H^+:-138O_2$. However, most anaerobic pathways of respiration, such as sulfate reduction, denitrification, and reduction of Fe oxides, would significantly increase TA (Liss 1992). Calcium carbonate dissolution/precipitation would also change TA and DIC in a ratio of 2:1. Many studies (Berner et al. 1970; Kempe 1982; Hoppema 1993; Smith and Hollibaugh 1997; Raymond et al. 2000) have either proposed or showed that sulfate reduction in sediment can be the dominant anaerobic pathway that creates a source of TA. For Georgia's estuary–marsh complexes, it has

Table 3. Summary of carbon fluxes in the SAB and its coastal salt marsh. All areal rates of marsh represent the values of per m^2 marsh. The total salt marsh area of the Southeastern United States, 457,050 ha (Reimold 1977), is used to convert the annual areal values to the annual total. Annual areal CO_2 degassing rate when marsh water is over marsh was estimated by adjusting the CO_2 degassing rate in the segment 5 of the Duplin River (445 g C m^{-2} of water yr^{-1}; Table 2) by a factor of ¼ (daily marsh inundation time, 6 h) and a factor of ½ (sluggish wind for the marsh water; Cai and Wang 1998). Annual areal CO_2 degassing rate with marsh water in creek bed was calculated by scaling the CO_2 degassing rate in the segment 5 of the Duplin River by a factor of 1/5 (ratio of water to marsh area in the Duplin River; Ragotzkie and Bryson 1955); this scaling converts per m^2 of water to per m^2 of marsh for comparison and extrapolation. The total inorganic carbon loss from marsh was calculated as the sum of DIC export from marsh and CO_2 degassing from marsh water and sediment.

Processes	Annual areal rates (g C m^{-2} yr^{-1})	Annual total ($\times 10^{12}$ g C yr^{-1})	Reference
Net primary production (NPP) in marsh	2025	9.3	Hopkinson (1988)
DIC export from marsh	156	0.7	This study
CO_2 degassing with marsh water over marsh	56	0.3	This study
CO_2 degassing with marsh water in creek bed	89	0.4	This study
CO_2 degassing from exposed marsh sediment	223–328	1.0–1.5	Morris and Whiting (1986)
Total inorganic carbon loss from marsh	524–629 (26–31% of NPP)	2.4–2.9	This study
DOC and POC export from marsh	260–1090	1.2–5.0	Chalmers et al. (1985); Hopkinson (1988)
DIC export from the SAB to the open ocean	29	2.6	Wang (2003); Cai et al. (2003)
CO_2 air–sea exchange (sea to air) in the SAB	30	2.7	Wang (2003); Cai et al. (2003)

also been argued that the addition of TA to estuarine water mainly results from sulfate reduction in ambient marsh sediment (Cai and Wang 1998). Alkalinity produced along with inorganic carbon released during anaerobic respiration may accumulate in marsh sediment pore water and create a significant source of DIC and TA to estuarine water via drainage and diffusion (Howarth and Giblin 1983; Cai et al. 1999, 2002; Neubauer and Anderson 2003). As far as we know, no studies have demonstrated that carbonate dissolution/precipitation is a major process that is responsible for the change of TA in Georgia's marsh-influenced estuaries. Consequently, anaerobic respiration in marshes may be the primary cause for the concurrent DIC and TA exports from the Duplin River. More paralleled patterns of DIC and TA exports from the upper two sections (Fig. 6b), where marsh effects were overwhelming, further support this conclusion. We therefore interpret TA export as a semiquantitative indicator of the cumulative effects of various anaerobic processes in the marshes of the Duplin River.

Marsh influences on the adjacent continental shelf—Cai and Wang (1998) estimated total riverine export of inorganic carbon to the U.S. southeastern Atlantic continental shelf, or the South Atlantic bight (SAB), to be 0.6×10^{12} g C yr^{-1}. However, DIC export from salt marshes to coastal waters via nonriverine marsh-dominated estuaries has not been documented prior to this study. DIC and CO_2 fluxes in the Duplin River provide direct evidence that Georgia salt marshes discharge inorganic carbon into adjacent estuaries. Wang (2003) also found a positive DIC concentration gradient from low to high salinity in summer and fall in Doboy and Sapelo Sounds (Fig. 2), suggesting that export of marsh-released DIC to coastal water must occur. By assuming the same eddy diffusion coefficient in Sapelo Sound as in the Duplin River (Eq. 2), he estimated the annual DIC export from Sapelo Sound to be 268 g C m^{-2} yr^{-1}, which is over twice the quantity exported from the Duplin River (109 g C m^{-2} yr^{-1}). Since the actual longitudinal diffusion coefficient in Sapelo Sound is unknown, uncertainty of this estimate will be higher than that for the Duplin River. To investigate whether DIC export from salt marshes has significant influence on the CO_2 system of the SAB, we estimated the areal marsh DIC export based on the Duplin River data and extrapolated it to the entire area of salt marshes of the southeastern U.S. (from Cape Hatteras, North Carolina, to West Palm Beach, Florida).

We first calculated the annual total net DIC export from the upper box of the Duplin River between Lumber Landing and Flume Dock or the ''marsh water'' box (Imberger et al. 1983; Chalmers et al. 1985). This DIC export (1.02×10^8 g C yr^{-1}) was then divided by the entire upper marsh area of 6.5×10^5 m^2 (Chalmers et al. 1985) to convert it to areal marsh export (156 g C m^{-2} yr^{-1}) for the purpose of extrapolation to the salt marshes of the entire SAB (Table 3). Similar to our previous estimates, uncertainty associated with taking averages in this calculation was about 20%. We assume that variation of longitudinal diffusion coefficient (Eq. 2) would introduce 10% uncertainty, and therefore we expect that the overall uncertainty in our estimate of areal DIC export from salt marshes is around 30%.

Our estimate of areal marsh DIC export is comparable to the estimate of 175 g C m^{-2} yr^{-1} for a salt marsh in North Inlet, South Carolina (Morris and Whiting 1986). Additionally, a similar estimate (194 g C m^{-2} yr^{-1}) has been reported for tidal freshwater marshes in Virginia (Neubauer and Anderson 2003). The total loss of inorganic carbon via DIC export and CO_2 degassing from the upper Duplin River water and from flooded and exposed marshes, which approximately represent the total respiration by heterotrophs in the marsh, accounts for 26–31% of net primary production in the marshes (Table 3). This is consistent with the previous finding that about 36% of the net primary production in the Duplin River's marsh is respired (Hopkinson 1988).

The extrapolated total net DIC export from the SAB salt marshes (0.7×10^{12} g C yr^{-1}) alone represents ca. 15% of annual sea-to-air CO_2 flux plus DIC export to the open ocean in the SAB (Table 3). Combined with the riverine export (0.6×10^{12} g C yr^{-1}; Cai and Wang 1998), the total land-side export of DIC (1.3×10^{12} g C yr^{-1}) accounts for ca. 25% of the total inorganic carbon fluxes in the SAB (Table 3). Although DIC export from the salt marshes represents only 10% of the marsh's net primary production (Table 3), we conclude that such an export is significant to the CO_2 dynamics in the SAB. Marsh export of inorganic carbon is one of the primary mechanisms that cause the SAB to be an annual CO_2 source to the atmosphere and an exporter of inorganic carbon to the open ocean (Cai et al. 2003; Wang 2003). Given 30–50% uncertainty in the CO_2 and DIC flux calculations, this conclusion still holds.

In the context of testing Odum's outwelling hypothesis, Chalmers et al. (1985) estimated areal marsh exports of organic carbon in the Duplin River to be 260 g C m^{-2} yr^{-1} (Table 3) based on the similar calculation performed in this study. They also found that the export showed a seasonal pattern with a summer maximum and winter minimum. Based on an analysis of marsh production and respiration rates, Hopkinson (1988), however, suggested that the Georgia salt marshes potentially export as much as 1090 g organic carbon m^{-2} yr^{-1}. Organic carbon export during storm/rain events may explain the difference (Chalmers et al. 1985). Note that organic carbon burial in marsh sediments is negligible in the budget consideration (Hopkinson 1988). In addition, higher total respiration than primary production in the nearshore water and sediment off Sapelo Island suggests that outwelling of organic carbon from the intertidal marsh must occur to subsidize the net system heterotrophy in shelf water (Hopkinson 1985).

We therefore argue that Georgia salt marshes outwell both organic and inorganic carbon to coastal waters. Dame (1994) also indicated net export of both organic and inorganic materials in 6 out of 10 systems on the Atlantic coast of North America. In South Africa, Winter et al. (1996) concluded that salt marshes were net exporters of both organic and inorganic carbon, but DIC flux was about 10 times the value of either POC or DOC export. Therefore, it seems to be common that marsh-dominated estuaries serve as a transport and transformation mechanism that delivers both organic and inorganic carbon released from salt marshes to the coastal waters (Fig. 1). Finally, since part of marsh-exported organic carbon must be respired in these estuaries, we argue that these estuaries are likely to be both apparently and actually net heterotrophic in nature. However, it must be noted that our system does not include ambient marsh primary producers. Otherwise, CO_2 fixation in the marshes would exceed CO_2 degassing plus DIC export, and the conclusion would be different (Table 3 and Fig. 8).

A marsh CO_2 pump—Georgia marsh systems are highly productive (Hopkinson 1988; Dai and Wiegert 1996) with annual net primary production almost one order of magnitude higher than any single export flux of either organic or inorganic carbon (Table 3 and Fig. 8). Such high annual primary production is able to support high respiration rates and organic and inorganic carbon exportations (Wiegert et al. 1981; Chalmers et al. 1985).

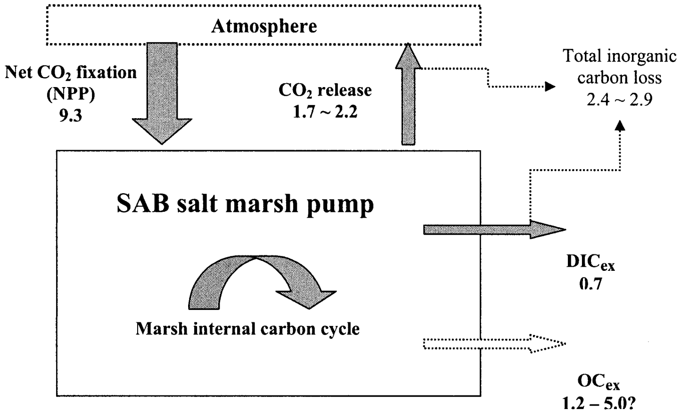

Fig. 8. Visualization of Table 3 and representation of the marsh CO_2 pump. Arrows represent the carbon fluxes into and out of the U.S. southeastern salt marshes. All numbers are annual values in 10^{12} g C yr^{-1} (Table 3). DIC_{ex} and OC_{ex} denote the export fluxes of inorganic and organic carbon from the salt marshes, respectively. Because organic carbon burial only accounts 1–2% of net primary production in the marshes (Hopkinson 1988), we chose to ignore this flux.

In summary, we propose a ''marsh CO_2 pump'' concept regarding carbon fixation and subsequent export to adjacent waters (Fig. 8). The seasonality of this pump prompts a seasonal progression of inorganic carbon signals in adjacent coastal systems. In spring and early summer, when marsh primary producers are at their annual maximum growth rate (Dame 1989), the marsh pumps in large amounts of CO_2 from the atmosphere by assimilating it into organic carbon through photosynthesis, while it pumps out only a small amount of carbon. This corresponds to a pump-in or accumulation stage. Consistently, the apparent net heterotrophy (ANH) and CO_2 oversaturation of the surface water in marsh-dominated estuaries are at their annual minima (Fig. 6). As the season proceeds, marsh primary production decreases while respiration increases. Therefore, the marsh pumps in less CO_2 from the atmosphere and pumps out more inorganic and organic carbon. Accordingly, the ANH, respiration, and CO_2 oversaturation in marsh-dominated estuaries are enhanced (Fig. 6 and Table 1). In late summer and fall, the marsh pumps out a significant amount of inorganic and organic carbon to adjacent estuaries and coastal waters. This results in an ANH peak, high respiration rates, and the highest degree of CO_2 oversaturation of the year in marsh-dominated estuaries (Table 1 and Fig. 6). The situation corresponds to a maximum pump-out or releasing stage. Marsh export of alkalinity also reaches the annual maximum as a result of intensive anaerobic respiration in marshes. In winter, primary production and respiration in the marsh are all at the annual low, and the pumping rates reduce both ways. The degree of the ANH and CO_2 oversaturation in marsh-dominated estuaries declines accordingly (Fig. 6).

Spatial and temporal variations of inorganic carbon in Georgia's riverine estuaries also support this marsh CO_2 pump concept (Cai and Wang 1998; Cai et al. 2000; Wang 2003). Furthermore, seasonal variation of surface water

$p\mathrm{CO}_2$ in the adjacent SAB generally matches that observed in marsh-dominated estuaries (Cai et al. 2003; Wang 2003). Therefore, we conclude that marsh processes play a critical role in maintaining the seasonal pace of carbon cycling in Georgia's coastal and continental shelf systems.

Implication for carbon sequestration—The overall marsh–estuary–shelf continuum is, however, still a net CO_2 sink when the large CO_2 fixation by marsh primary producers is included in the picture (Table 3 and Fig. 8). The mechanisms proposed here provide an efficient means for ocean carbon sequestration of atmospheric CO_2. At one end of this system, a large amount of atmospheric CO_2 is fixed by the marsh primary producers; at the other end, inorganic and organic carbon is exported to the ocean. This marsh-regulated biological pump mechanism may have important implications for global carbon cycling and CO_2 budgets if a large fraction of global coastal wetlands and their adjacent water systems behaves similarly to the systems investigated in this study.

While 80% of the 5.9×10^9 m^2 of salt marshes on the U.S. Atlantic coast are located in the SAB (Reimold 1977), they account for only a few percent of total global salt marsh area. Woodwell et al. (1973) estimated a total global marsh area (including mangrove) of 3.8×10^{11} m^2 by extrapolating the ratio of marshes to coastline in the United States to a global level. While the estimate of Woodwell et al. (1973) may be on the high end, the vast amount of marshes bordering the SAB is certainly not unique, although it may be rare globally. The conclusions drawn here should, therefore, be of general interest to studies of carbon cycles in other shelves.

References

Berner, R. A., M. R. Scott, and C. Thomlinson. 1970. Carbonate alkalinity in the pore waters of anoxic marine sediments. Limnol. Oceanogr. **15:** 544–549.

Cai, W.-J., L. R. Pomeroy, M. A. Moran, and Y. Wang. 1999. Oxygen and carbon dioxide mass balance for the estuarine-intertidal marsh complex of five rivers in the southeastern U.S. Limnol. Oceanogr. **44:** 639–649.

———, and Y. Wang. 1998. The chemistry, fluxes, and sources of carbon dioxide in the estuarine waters of the Satilla and Altamaha River, Georgia. Limnol. Oceanogr. **43:** 657–668.

———, Z. Wang, and Y. Wang. 2003. The role of marsh-dominated heterotrophic continental margins in transport of CO_2 between the atmosphere, the land-sea interface and the ocean. Geophys. Res. Lett. **30(16):** 1849, doi:10.1029/2003GL017633.

———, W. J. Wiebe, Y. Wang, and J. E. Sheldon. 2000. Intertidal marsh as a source of dissolved inorganic carbon and a sink of NO_3^- in the Satilla River-estuarine complex in the southeastern U.S. Limnol. Oceanogr. **45:** 1743–1752.

———, P. Zhao, S. M. Theberge, A. Witter, Y. Wang, and G. Luther, III. 2002. Porewater redox species, pH and $p\mathrm{CO}_2$ in aquatic sediments—electrochemical sensor studies in Lake Champlain and Sapelo Island. *In* M. Taillefert and T. F. Rozan [eds.], Environmental electrochemistry: Analyses of trace element biogeochemistry. American Chemical Society Symposium Series 811.

Chalmers, A. G., R. G. Wiegert, and P. L. Wolf. 1985. Carbon balance in a salt marsh: Interactions of diffusion export, tidal deposition, and rainfall-caused erosion. Estuar. Coast. Shelf Sci. **21:** 757–771.

Childers, D. L. 1994. Fifteen years of marsh flumes: A review of marsh-water column interactions in southeastern USA estuaries, pp. 277–293. *In* W. J. Mitsch [ed.], Global wetlands: Old world and new. Elsevier.

———, J. W. Day, Jr., and H. N. Mckellar, Jr. 2000. Twenty more years of marsh and estuarine flux studies: Revisiting Nixon (1980), pp. 391–423. *In* M. P. Weinstein and D. A. Kreeger [eds.], Concepts and controversies in tidal marsh ecology. Kluwer Academic.

Dai, T., and R. G. Wiegert. 1996. Ramet population dynamics and net aerial primary productivity of *Spartina alterniflora.* Ecology **77:** 276–288.

Dame, R. F. 1989. The importance of *Spartina alterniflora* to Atlantic coast estuaries. Crit. Rev. Aquat. Sci. **1:** 639–660.

———. 1994. The net flux of materials between marsh-estuarine systems and the sea: The Atlantic coast of the United States, pp. 295–305. *In* W. J. Mitsch [ed.], Global wetlands: Old world and new. Elsevier.

———, and others. 1986. The outwelling hypothesis and North Inlet, South Carolina. Mar. Ecol. Prog. Ser. **33:** 217–229.

DeGrandpre, M. D., G. D. Olbu, C. M. Beatty, and T. R. Hammar. 2002. Air–sea CO_2 fluxes on the U.S. Middle Atlantic Bight. Deep-Sea Res. II **49:** 4355–4367.

Feely, R. A., R. Wanninkhof, H. B. Milburn, C. E. Cosca, M. Stapp, and P. P. Murphy. 1998. A new automated underway system for making high precision $p\mathrm{CO}_2$ measurements onboard research ships. Anal. Chim. Acta **377:** 185–191.

Frankignoulle, M., and A. V. Borges. 2001*a*. European continental shelf as a significant sink for atmospheric carbon dioxide. Glob. Biogeochem. Cycles **15:** 569–576.

———, and ———. 2001*b*. Direct and indirect $p\mathrm{CO}_2$ measurements in a wide range of $p\mathrm{CO}_2$ and salinity values (the Scheldt Estuary). Aquat. Geochem. **7:** 267–273.

———, I. Bourge, and R. Wollast. 1996. Atmospheric CO_2 fluxes in a highly polluted estuary (the Scheldt). Limnol. Oceanogr. **41:** 365–369.

———, and others. 1998. Carbon dioxide emission from European estuaries. Science **282:** 434–436.

Gattuso, J.-P., M. Frankignoulle, and R. Wollast. 1998. Carbon and carbonate metabolism in coastal aquatic ecosystems. Annu. Rev. Ecol. Syst. **29:** 405–434.

Gran, G. 1952. Determination of the equivalence point in potentiometric titrations. Part II. Analyst **77:** 661–671.

Hopkinson, C. S. 1985. Shallow-water and pelagic metabolism: Evidence of heterotrophy in the near-shore Georgia Bight. Mar. Biol. **87:** 19–32.

———. 1988. Patterns of organic carbon exchange between coastal ecosystems the mass balance approach in salt marsh ecosystems, pp. 122–154. *In* B.-O. Jansson [ed.], Coastal-offshore ecosystem interactions. Springer.

Hoppema, J. M. J. 1993. Carbon dioxide and oxygen disequilibrium in a tidal basin (Dutch Wadden Sea). Neth. J. Sea Res. **31:** 221–229.

Howarth, R. W., and A. Giblin. 1983. Sulfate reduction in the salt marshes at Sapelo Island, Georgia. Limnol. Oceanogr. **28:** 70–82.

Imberger, J., and others. 1983. The influence of water motion on the distribution and transport of materials in a salt marsh estuary. Limnol. Oceanogr. **28:** 201–214.

Kemp, W. M., E. Smith, M. Marvin-Dipasquale, and W. R. Boynton. 1997. Organic carbon balance and net ecosystem metabolism in Chesapeake Bay. Mar. Ecol. Prog. Ser. **150:** 229–248.

Kempe, S. 1982. Long term records of CO_2 pressure fluctuations in fresh waters, pp. 91–332. *In* E. T. Degens [ed.], Transport of carbon and minerals in major world rivers, Pt. 1. Mitt. Geol.-Palaont. Inst. Univ. Hamburg, SCOPE/UNEP Sonderbd. 52.

KÖRTZINGER, A., AND OTHERS. 2000. The international at-sea intercomparison of $f\mathrm{CO}_2$ systems during the R/V Meteor cruise 36/1 in the North Atlantic Ocean. Mar. Chem. **72:** 171–192.

LISS, S. M. [ED.]. 1992. An introduction to marine biogeochemistry. Wiley.

MORRIS, J. T., AND G. J. WHITING. 1986. Emission of gaseous carbon dioxide from salt-marsh sediments and its relation to other carbon losses. Estuaries **9:** 9–19.

NEUBAUER, S. C., AND I. C. ANDERSON. 2003. Transport of dissolved inorganic carbon from a tidal freshwater marsh to the York River estuary. Limnol. Oceanogr. **48:** 299–307.

NIXON, S. W. 1980. Between coastal marshes and coastal waters—a review of twenty years of speculation and research on the role of salt marshes in estuarine productivity and water chemistry, p. 437–525. *In* P. Hamilton and K. B. MacDonald [eds.], Estuarine and wetland processes. Plenum.

ODUM, E. P. 1968. A research challenge: Evaluating the productivity of coastal and estuarine water, p. 63–64. *In* Proceedings Second Sea Grant Conference, Univ. Rhode Island.

POMEROY, L. R., J. E. SHELDON, W. M. SHELDON, J. O. BLANTON, JR., J. AMFT, AND F. PETERS. 2000. Seasonal changes in microbial processes in estuarine and continental shelf waters of the South-eastern U.S.A. Estuar. Coast. Shelf Sci. **51:** 415–428.

———, L. R. SHENTON, R. D. H. JONES, AND R. J. REIMOLD. 1972. Nutrient flux in estuaries. *In* Nutrient and Eutrophication, Special Symposia, Vol. 1, Am. Soc. Limnol Oceanogr.

———, AND R. G. WIEGERT [EDS.] 1981. The ecology of a salt marsh. Springer.

RAGOTZKIE, R. A., AND R. A. BRYSON. 1955. Hydrography of the Duplin River, Sapelo Island, Georgia. Bull. Mar. Sci. **5:** 297–314.

RAYMOND, P. A., J. E. BAUER, AND J. J. COLE. 2000. Atmospheric CO_2 evasion, dissolved inorganic carbon production, and net heterotrophy in the York River estuary. Limnol. Oceanogr. **45:** 1707–1717.

———, N. F. CARACO, AND J. J. COLE. 1997. Carbon dioxide concentration and atmospheric flux in the Hudson River. Estuaries **20:** 381–390.

REIMOLD, R. J. 1977. Mangals and salt marshes of eastern United States. *In* V. J. Chapman [ed.], Wet coastal ecosystems, Vol. 1. Elsevier.

SMITH, S. V., AND J. T. HOLLIBAUGH. 1993. Coastal metabolism and the oceanic organic carbon balance. Rev. Geophys. **31:** 75–89.

———, AND ———. 1997. Annual cycle and interannual variability of ecosystem metabolism in a temperate climate embayment. Ecol. Monogr. **67:** 509–533.

TAYLOR, C. D., AND B. L. HOWES. 1994. Effect of sampling frequency on measurements of seasonal primary production and oxygen status in near-shore coastal ecosystems. Mar. Ecol. Prog. Ser. **108:** 193–203.

TEAL, J. M. 1962. Energy flows in the salt marsh ecosystem of Georgia. Ecology **43:** 614–624.

TSUNOGAI, S., S. WATANABE, AND T. SATO. 1999. Is there a ''continental shelf pump'' for the absorption of atmospheric CO_2? Tellus **51B:** 701–712.

WANG, Z. A. 2003. Biogeochemical changes of chemical signals in the Georgia ''land-to-ocean continuum.'' Ph.D. dissertation, Univ. Georgia.

WANNINKHOF, R. 1992. Relationship between wind speed and gas exchange over the ocean. J. Geophys. Res. **97:** 7373–7382.

WEISS, R. F. 1974. Carbon dioxide in water and seawater: The solubility of a non-ideal gas. Mar. Chem. **2:** 203–215.

WIEGERT, R. G., A. G. CHALMERS, AND P. F. RANDERSON. 1983. Productivity gradients in salt marshes: The responses of *Spartina alterniflora* to experimentally manipulated soil water movement. Oikos **43:** 1–6.

———, R. R. CHRISTIAN, AND R. L. WETZEL. 1981. A model view of the marsh, p. 183–218. *In* L. R. Pomeroy and R. G. Wiegert [eds.], The ecology of a salt marsh. Springer.

WINTER, P. E. D., T. A. SCHLACHER, AND D. BAIRD. 1996. Carbon flux between estuary and the ocean: A case for outwelling. Hydrobiologia **337:** 123–132.

WOODWELL, G. M., P. H. RICH, AND C. A. S. HALL. 1973. Carbon in estuaries. *In* G. M. Woodwell and E. V. Pecan [eds.], Carbon and the biosphere. U.S. Atomic Commission.

Received: 15 April 2003
Accepted: 1 October 2003
Amended: 21 October 2003