

## Oxygen and carbon dioxide mass balance for the estuarine–intertidal marsh complex of five rivers in the southeastern U.S.

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### *Abstract*

We measured dissolved  $O_2$  concentrations,  $pCO_2$  values, and respiratory rates in five estuaries of the southeastern U.S. in October 1995 and July 1996. In the low-salinity sections of the coastal plain rivers, dissolved  $O_2$  saturation states were typically only 50%, while  $pCO_2$  values were over 4,000  $\mu\text{atm}$ . Respiratory rates measured concurrently in estuarine water averaged 8 and 23  $\text{mmol m}^{-3} \text{d}^{-1}$  in October 1995 and July 1996, but they showed little variability either within or among the five estuaries. Benthic chamber incubations in the adjacent intertidal marshes indicated fluxes of 30–40  $\text{mmol m}^{-2} \text{d}^{-1}$  and 50–120  $\text{mmol m}^{-2} \text{d}^{-1}$  for  $O_2$  and total dissolved inorganic carbon (DIC), respectively. For the Satilla River estuary, simple calculations revealed that neither respiratory activity in estuarine waters and sediments nor any other within-estuary process (not including the intertidal marsh system) was sufficient to account for the observed  $O_2$  concentrations and  $pCO_2$  values. Dissolved oxygen concentrations in four other southeastern U.S. estuaries fit the same general pattern as the Satilla, and likewise, within-estuary processes could not explain observed gas concentrations. Measured  $O_2$  concentrations,  $pCO_2$  values, pelagic respiratory rates, and benthic fluxes were used to construct a mass-balance model, focusing on the influence of the extensive intertidal marshes on  $O_2$  and  $CO_2$  mass balance and water–atmosphere gas exchange in the five estuaries. Results indicate that respiratory activity in the sediments and overlying water of the marshes during high tide leaves a signal that is funneled back to the estuary during ebb tide and can account for the estuarine gas concentrations and fluxes. Both experimental and modeling approaches argue that the intertidal marshes of the southeastern U.S. export considerable amounts of inorganic respiratory products to the estuaries and that “outwelling” of organic matter to the estuaries is a minor process by comparison. The DIC exported to the coastal ocean, however, is only a small fraction of the total gas mass flow between the marsh, estuary, and atmosphere.

Early recognition of coastal intertidal marshes as highly productive ecosystems led to the hypothesis that marshes contribute significant amounts of organic carbon to estuaries and the coastal ocean (Teal 1962; Odum 1968, 1980). This hypothesis, based primarily on the coastal marshes of Georgia, was further supported by observations of estuarine oxygen deficits (Ragotzkie 1959; Pomeroy et al. 1972; Frankenberg 1975; Frankenberg and Shimmel 1975). The outwelling hypothesis was later challenged, at first because there were insufficient supporting data (Nixon 1980) and later because new data and more detailed models of estuaries did not reveal large fluxes of organic matter from marshes (Woodwell et al. 1977; Wiegert et al. 1981; Chalmers et al. 1985; Childers et al. 1993). For example, the model of Wiegert et al. (1981) suggested a net export of about 25% of

primary production from the Georgia marshes, yet empirical flume studies showed a 25% import of organic matter from the estuary to the marshes (Chalmers et al. 1985). Stable isotope analyses focusing specifically on diets of estuarine consumers indicated a significant role for intertidal marsh plants in estuarine systems (Peterson and Howarth 1987) but could not address the broader issue of net exchange between the marsh and estuary. Similar gaps can be found in other estuarine studies, and Dame’s (1994) summary of net export in marsh–estuarine systems on the Atlantic coast of North America indicated net export of both organic and inorganic materials in 6 out of 10 systems, implying that marshes are simultaneously net autotrophic and net heterotrophic.

The validity of the outwelling hypothesis is just one component of the larger issue of the trophic status of estuaries, particularly the importance of estuarine heterotrophy on a global basis (Smith and Hollibaugh 1993; Kemp et al. 1997). Although still the subject of some controversy, the pendulum of opinion seems to have swung toward the view that many estuaries are net heterotrophic (Smith 1991; Smith and Hollibaugh 1997), notwithstanding eutrophication trends that may shift this balance (Kemp et al. 1997). While intertidal marshes are one possible source of organic matter to heterotrophic estuaries, organic matter of riverine, marine, and es-

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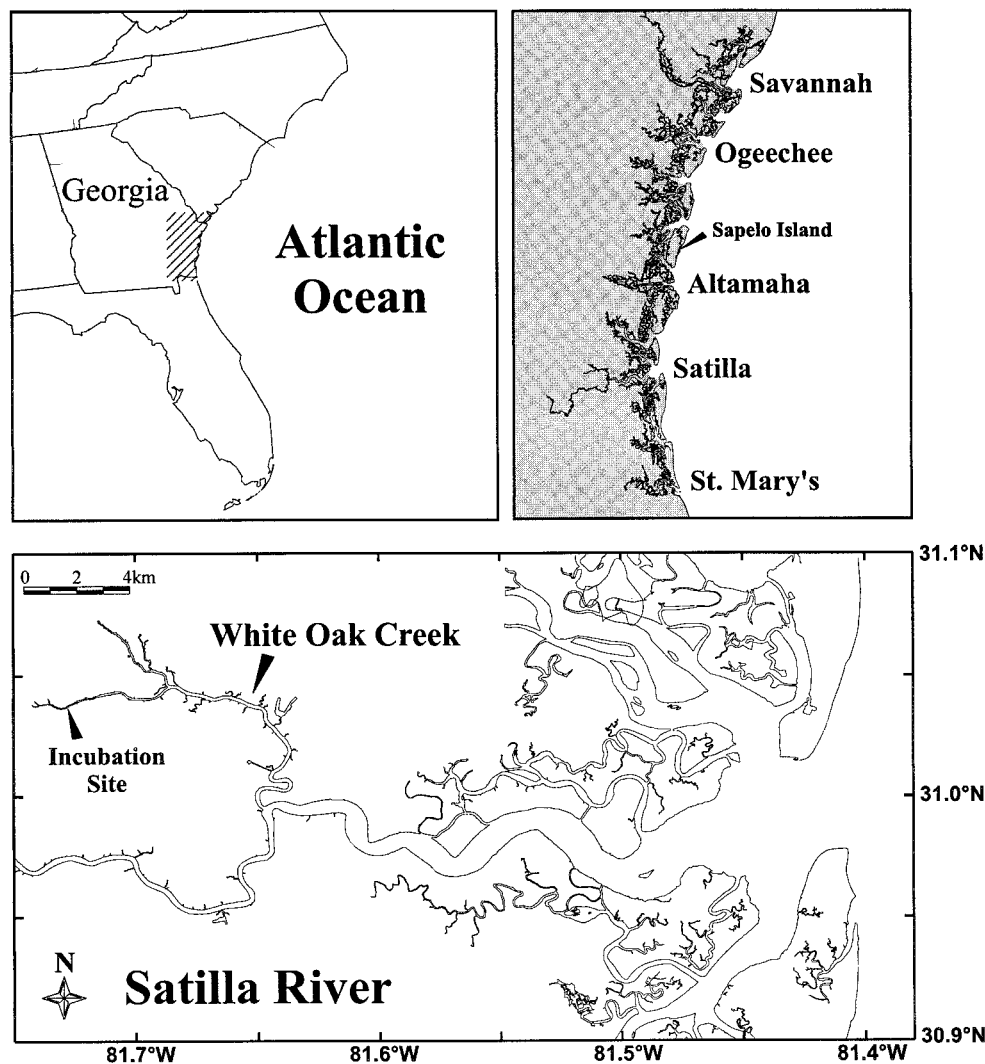


Fig. 1. Coastline of the southeastern U.S. and locations of the five Georgia estuaries and intertidal marsh sites.

tuarine origin can also fuel estuarine respiration (Smith and Hollibaugh 1993).

Because precise measurements of the fluxes of all categories of living and nonliving organic matter are difficult to achieve, we have tried to reevaluate the question of estuarine-marsh interactions from the viewpoint of oxygen and carbon dioxide exchanges between marsh, estuary, and atmosphere. Our approach uses  $O_2$  and  $CO_2$  concentrations in estuarine waters as integrated measures of production, respiration, and gas exchange in the estuary-intertidal marsh complex. Our evaluation makes a distinction between organic and inorganic materials and differentiates between the estuary and coastal ocean as the recipient of outwelled material. This study is also unique in that it includes estuarine systems (and associated intertidal marshes) throughout a wide salinity range. By examining overall gas exchanges and evaluating them in the context of a mass-balance model, we also provide a valuable comparison with individual measurements of specific processes in the coastal marshes that span several decades.

#### Site description and methods

The coast of Georgia is in the middle of a bight that extends from Cape Hatteras, North Carolina ( $35^\circ N$ ), to Cape Canaveral, Florida ( $28^\circ N$ ), covering an area of  $90,600 \text{ km}^2$  (Menzel 1993). Five rivers are evenly distributed along the coast, and a series of barrier islands and extensive salt marshes border the sea (Fig. 1). The five Georgia rivers can be divided into two types, those originating in the piedmont province of the southeastern U.S. (the Savannah and Altamaha) and those originating on the coastal plain province (the Satilla and St. Marys). The fifth river (the Ogeechee) has both piedmont and coastal plain influence. Water transported by rivers with extensive piedmont drainage has high carbonate content and relatively high pH. Water transported by rivers originating in the coastal plain is "blackwater," with very high DIC content (mostly humic substances) and very low pH (Beck et al. 1974; Cai and Wang 1998; Cai et al. 1998). The flushing times (total volume of freshwater divided by the freshwater input) for these estuaries range

from 3–4 d for the piedmont rivers to 25–30 d for the coastal plain rivers (Moran et al. 1999; Alber and Sheldon pers. comm.). Mean flow rates of these rivers are 344, 394, 86, 65, and 19 m<sup>3</sup> s<sup>-1</sup>, respectively, for the Savannah, Altamaha, Ogeechee, Satilla, and St. Marys.

An important feature of these estuaries is that they are surrounded by extensive areas of intertidal marshes. These marshes and creeks are flooded by estuarine waters twice a day and have negligible freshwater input. All of the marshes in Georgia, as well as adjacent marshes in South Carolina and Florida, are very similar in productivity, sediment type, tidal range, and climatic regime. In a comparison of marsh–water exchange data from flume studies throughout the region, Childers (1994) found that studies within the St. Marys–Satilla watersheds did not differ markedly from those in the northern Altamaha delta. Thus, we expect greater differences in rates of material exchange along the salinity gradient of the estuaries than between estuaries at any given salinity range and therefore, assemble data from the Georgia coast on the basis of salinity rather than north–south geography. Except for the Savannah River and one major dam on a tributary of the Altamaha, all the rivers are relatively pristine. The Georgia coastal plain is, however, subject to considerable anthropogenic pressure for development in terms of both industrial growth and increased human population. Thus, an evaluation of the current status of the estuaries is of practical as well as basic interest.

For an analysis of mass balance of oxygen and carbon dioxide, we have drawn data from the literature as well as obtained new data. The new data reported here were collected during research cruises on the RV *Blue Fin* during October 1995 and July 1996 and from land-based operations near Sapelo Island and along the Satilla River estuary during July and August 1997.

To measure respiratory rates of estuarine water, sets of five 125-ml glass bottles were filled to overflowing from a Niskin bottle. Bottles were capped free of head space and placed in a dark incubator at in situ water temperature for approximately 12 h, then fixed with Winkler reagents. A duplicate set of five bottles was fixed at the time of sample collection to serve as the zero-time measure for respiration calculations and as the measure of ambient dissolved oxygen in the estuary. Precision Winkler titrations were performed as described by Pomeroy et al. (1994). Values for *p*CO<sub>2</sub> in estuarine waters were calculated from DIC and pH measurements by methods detailed in Cai and Wang (1998). All pH samples were measured on shipboard without adding preservative, while DIC samples were preserved with HgCl<sub>2</sub> and measured 1–2 weeks later. Values thus calculated compare well with direct *p*CO<sub>2</sub> measurements made during the same month 1 yr later (Cai unpubl. data).

Incubations to determine benthic O<sub>2</sub> and carbon fluxes were conducted at two intertidal marsh sites. The first site was a short-form *Spartina* marsh adjacent to the University of Georgia Marine Institute on Sapelo Island (31°22.7'N, 81°16.8'W, with northern Altamaha delta influence) and was accessible from land by a boardwalk; this site was sampled in 1997 on 27 August (1630–1900 h) for O<sub>2</sub> flux measurements and on 28 August (1700–2000 h) for DIC flux measurements. The water depth above the short-form *Spartina*

during high tide was about 40 cm, and there was a 3-h period of flooding, during which the benthic chambers were deployed. Four chambers (diameter = 14 cm, water height = 7–10 cm) made of stainless steel tubing with a sharp bottom were inserted into the sediments to a 3–4-cm depth. The chambers had polyvinyl chloride caps with an electrode and/or sampling port covered loosely by a rubber plug. Two rubber bulbs on the cap were used as stirrers by manual squeezing. In the first deployment, a YSI electrode was used to monitor O<sub>2</sub> concentration inside each chamber, and water samples for DIC analysis were collected at the beginning and end of the incubation. The chambers were stirred for 15 s while O<sub>2</sub> readings were taken, which occurred at 15–30-min intervals. In the second deployment, water samples for DIC analysis were collected every 0.5 h, and the chambers were stirred for 15 s immediately prior to each sampling. The 6-ml water samples were preserved with HgCl<sub>2</sub> and analyzed later at our laboratory in Athens, Georgia. All reported measurements are of gross respiratory rate in the dark. The marsh waters external to the chamber were relatively still, except toward the end of the incubation as the tide was beginning to ebb. Outside overlying marsh water was allowed to flow into the chambers to replace the sample volumes removed; the total volume of water removed for analysis was <1% of the chamber volume. We also measured the O<sub>2</sub> concentration in waters overlying the marsh at random sites selected within a 100- × 100-m<sup>2</sup> area surrounding the incubation site. Oxygen saturation in these samples was measured with a microelectrode in a flow-through cell.

The second benthic chamber incubation site was on the bank of a small tributary to White Oak Creek (31°2.2'N, 81°43.5'W) (Fig. 1), in a low-salinity region of the Satilla estuary; this site was sampled in 1997 on 3 October (1030–1300 h) for O<sub>2</sub> flux measurements. The site was vegetated by tall-form *Spartina alterniflora* and was accessed by a small boat. During the incubation, water samples for oxygen measurements were collected from the chambers in plastic syringes and stored on ice for 1–3 h until analysis. Oxygen concentrations were subsequently measured by injecting the syringe sample into a microelectrode flow-through cell. The microelectrode was calibrated in the same cell in moist air several times during measurements, and the uncertainties in O<sub>2</sub> measurements are about ~3%.

## Results

In all of the Georgia estuaries, we found dissolved oxygen concentrations approaching saturation in the high-salinity regions near the mouths of the estuaries. For the piedmont rivers (the Savannah and Altamaha), oxygen concentration was somewhat depressed at intermediate salinities, but it again approached saturation in the zero-salinity regions (Fig. 2a). For the two coastal plain rivers (the Satilla and St. Marys), dissolved oxygen concentrations continued to decline throughout the estuary and were lowest in the 0–12‰ region. We also found a marked rise in *p*CO<sub>2</sub> with decreasing salinity in the Satilla River (data not available for the other rivers), with the maximum *p*CO<sub>2</sub> values measured at 2–5‰ in July 1996 (Fig. 2b). The pelagic respiration rates mea-

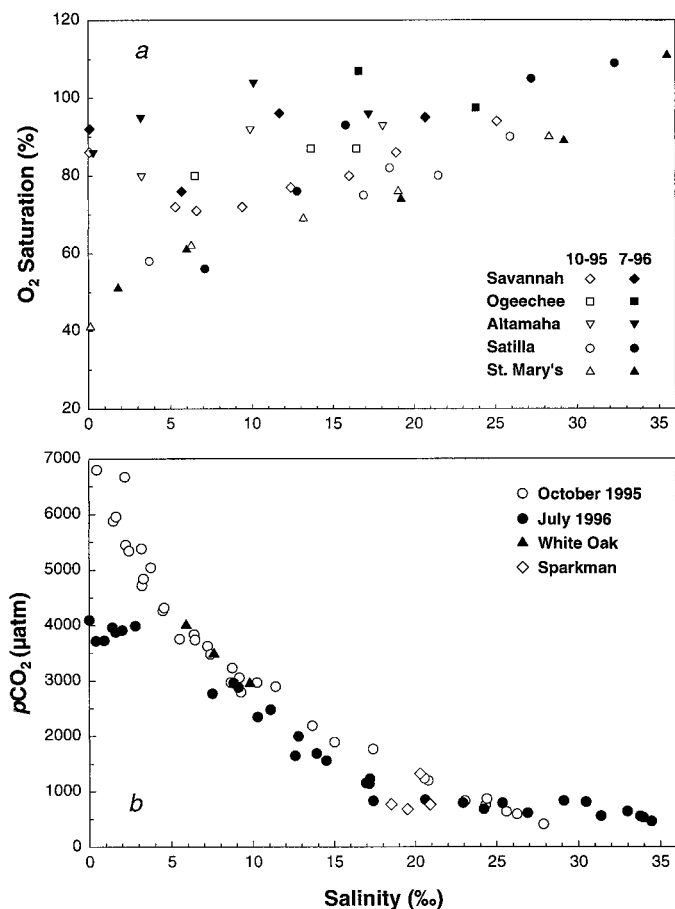


Fig. 2. Dissolved O<sub>2</sub> concentrations vs. salinity for five Georgia estuaries (a) and pCO<sub>2</sub> values vs. salinity for the Satilla estuary (b) in October 1995 and July 1996 (including tributaries White Oak Creek and Sparkman Creek in July 1996).

sured during the October 1995 and July 1996 cruises showed no pattern along the salinity gradient for any of the rivers and no significant differences between rivers; average values for the two cruises were  $8.2 \pm 1$  and  $22.7 \pm 1.7$  (SE) mmol m<sup>-3</sup> d<sup>-1</sup>, respectively (Table 1).

For the benthic chamber incubations, a linear relationship with time was observed for both O<sub>2</sub> and DIC concentrations (data not shown), and fluxes were calculated from linear regressions of these plots. The benthic fluxes measured at the Sapelo Island salt marsh are within the range of the historical data from this site (Table 2), and differences are of the magnitude expected for spatial and seasonal variation within a system. DIC flux appears to be higher than O<sub>2</sub> flux, although these measurements were made on sequential days at slightly different locations in the marsh. Rates of benthic gas flux at the White Oak Creek marsh were similar to the rates measured in the Sapelo Island marsh (Table 2). Dissolved O<sub>2</sub> concentration in the stratified water overlying the Sapelo marsh varied with time of day and with location and depth of the sample. Oxygen saturation in early morning averaged  $34 \pm 3\%$  ( $n = 5$ ) but approached zero in localized areas; saturation in the late afternoon averaged  $76 \pm 4\%$  ( $n = 6$ ). The initial oxygen concentrations in the benthic chamber

Table 1. Mean pelagic microbial respiratory rates for five Georgia estuaries in October 1995 and July 1996, including tidal fresh-water regions. Means of individual estuaries were not significantly different from the grand mean. Units are mmol O<sub>2</sub> m<sup>-3</sup> d<sup>-1</sup>  $\pm$  1 SE. The full data set can be accessed at <http://lmer.marsci.uga.edu>.

Estuary	October 1995		July 1996	
	Mean	<i>n</i>	Mean	<i>n</i>
Savannah	$7.4 \pm 0.7$	12	$21.8 \pm 4.1$	7
Ogeechee	$10.3 \pm 5.3$	5	$28.6 \pm 13.2$	3
Altamaha	$10.1 \pm 2.6$	7	$22.8 \pm 3.4$	8
Satilla	$6.0 \pm 1.7$	10	$24.2 \pm 7.4$	8
St. Marys	$10.8 \pm 1.2$	5	$20.9 \pm 1.2$	7
All estuaries	$8.2 \pm 1.0$	39	$22.7 \pm 1.7$	33

incubations at the White Oak Creek marsh represented average saturations of  $68 \pm 2\%$  ( $n = 8$ ; approximately 1200 h).

Gas transfer across the air–water interface was estimated by the stagnant layer model (Broecker and Peng 1982; Smethie et al. 1985). Accordingly, the influx of O<sub>2</sub> across the air–water interface was calculated as

$$F(\text{O}_2) = K_T \{ [\text{O}_2(\text{saturated})] - [\text{O}_2(\text{water})] \} \\ = K_T K_{\text{O}_2} \{ p\text{O}_2(\text{air}) - p\text{O}_2(\text{water}) \} \quad (1)$$

and the efflux of CO<sub>2</sub> as

$$F(\text{CO}_2) = K_T \{ [\text{CO}_2(\text{water})] - [\text{CO}_2(\text{saturated})] \} \\ = K_T K_{\text{CO}_2} \{ p\text{CO}_2(\text{water}) - p\text{CO}_2(\text{air}) \} \quad (2)$$

Here,  $K_{\text{O}_2}$  and  $K_{\text{CO}_2}$  are the solubility constants for O<sub>2</sub> and CO<sub>2</sub>, respectively (Weiss 1970, 1974). At a salinity of 5‰,  $K_{\text{O}_2} = 1.1 \text{ mol m}^{-3}\text{-atm}$  and  $K_{\text{CO}_2} = \sim 28 \text{ mol m}^{-3}\text{-atm}$ . This nearly 28-fold difference in solubility constants between O<sub>2</sub> and CO<sub>2</sub> is important for understanding the mass balance between O<sub>2</sub> flux and CO<sub>2</sub> flux. For example, field data at a salinity of 5‰ in the Satilla estuary show that the value of the term  $\{ p\text{O}_2(\text{air}) - p\text{O}_2(\text{water}) \}$  (which equals 0.1 atm) is about 28 times the value of  $\{ p\text{CO}_2(\text{water}) - p\text{CO}_2(\text{air}) \}$  (which equals 0.004 atm) (Fig. 2a,b). Therefore, fluxes of the two gases are expected to be similar.

$K_T$  represents the gas transfer velocity. In the Pee Dee River, South Carolina, where conditions are similar to those in Georgia, the gas transfer velocity was estimated by El-singer and Moore (1983) to be between 2.1 and 4.1 m d<sup>-1</sup> using <sup>222</sup>Rn technology. A similar value was used by Frankignoulle et al. (1996) in the Scheldt Estuary, and a mean of 4 m d<sup>-1</sup> was reported by Broecker and Peng (1982) and Smethie et al. (1985) for the open ocean. Ideally, one should correlate gas flux to local wind speed (Wanninkhof 1992). However, a gas transfer velocity of 2.1 m d<sup>-1</sup> is a reasonable and maybe conservative estimate for our estuaries given the average physical conditions (see table 1 in El-singer and Moore 1983) and was assumed for the purposes of calculating both CO<sub>2</sub> and O<sub>2</sub> fluxes in this study.

The air–water fluxes of O<sub>2</sub> and CO<sub>2</sub> over the whole estuary, calculated based on Eq. 1 and 2 using O<sub>2</sub> and pCO<sub>2</sub> data from July 1996 (Fig. 2), are presented in Fig. 3. Fluxes of both gases are very high in low-salinity waters, with the maximum at about 5‰.

Table 2. Benthic O<sub>2</sub> and CO<sub>2</sub> fluxes over flooded intertidal marsh sediments at Sapelo Island and White Oak Creek, Georgia. O<sub>2</sub> and DIC fluxes were measured on sequential days at slightly different locations in the marsh. All measurements were made during summer, except those of Teal and Kanwisher (1961), which were made during spring.

Location	% S	Benthic flux		Reference
		(mmol O <sub>2</sub> m <sup>-2</sup> d <sup>-1</sup> )	(mmol C m <sup>-2</sup> d <sup>-1</sup> )	
Sapelo marsh, short-form <i>Spartina</i>	28.8	34.0–41.3 (n = 4)	53.6–126 (n = 4)	This study
White Oak Creek, tall-form <i>Spartina</i>	10	40.2 ± 4.2 (n = 8)		This study
Sapelo marsh	25–29	30 (n = 29)		Pomeroy 1959
Lab incubation	25–29	55.1		Teal and Kanwisher 1961
Sapelo marsh	25–29	89.0–67.7		Teal and Kanwisher 1961

## Discussion

*O<sub>2</sub> and CO<sub>2</sub> signals in the Satilla River estuary*—Our data sets for gas concentrations and fluxes are most complete for the Satilla River, and we begin with a detailed analysis of this estuarine system. The low-salinity zone of the Satilla can be characterized by low dissolved O<sub>2</sub> concentrations (Fig. 2a) and very high pCO<sub>2</sub> values (Fig. 2b). pCO<sub>2</sub> values as high as 2,000 μatm have been seen previously in a number of rivers worldwide, although values >4,000 μatm in estuarine waters have rarely been reported (Kempe et al. 1991). An extremely high pCO<sub>2</sub> value (5,700 μatm) and corresponding CO<sub>2</sub> flux to the atmosphere was reported for the Scheldt Estuary at a salinity of 5‰ (Frankignoulle et al. 1996). Likewise, we observed pCO<sub>2</sub> values >6,000 μatm at salinities of 0–10‰ in the Satilla River in October 1995. pCO<sub>2</sub> values in the low-salinity regions were lower in July 1996, but nonetheless, they approached 4,000 μatm. A limited set of samples collected from the Satilla River estuary in February 1997 (during very high river flow) included pCO<sub>2</sub> values as high as 6,000 μatm at the head of tide (located 60 km upriver from the start of the zero-salinity zone) and 5,000 μatm in the low-salinity range of the estuary.

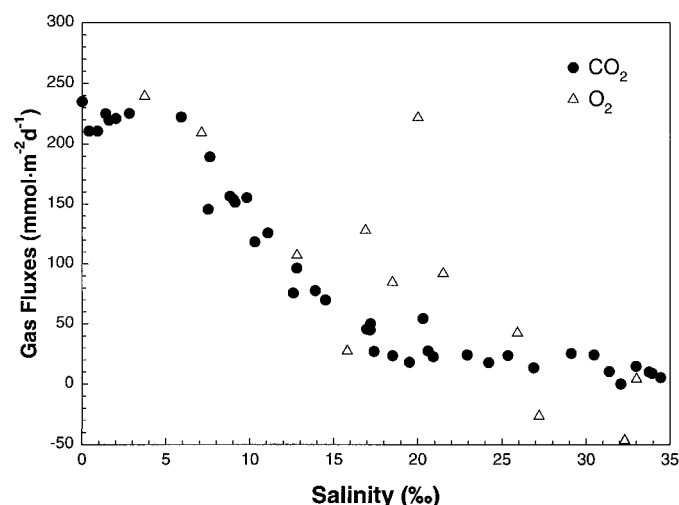


Fig. 3. Atmospheric fluxes of O<sub>2</sub> and CO<sub>2</sub> in the Satilla River estuary as a function of salinity (assuming  $K_T = 2.1 \text{ m d}^{-1}$ ).

Thus, the very high pCO<sub>2</sub> values and water-to-air CO<sub>2</sub> fluxes reported here and by Cai and Wang (1998) are characteristic of the Satilla River estuary. The high pCO<sub>2</sub> values and CO<sub>2</sub> fluxes in the Scheldt were measured downstream of Antwerp, in a highly polluted section of the river, and were likely related to respiration of organic pollutants (Frankignoulle et al. 1996). The Satilla, in contrast, is an essentially pristine river with extensive and highly productive intertidal marshes.

*Coupling respiratory rates and gas concentration data in the Satilla River estuary*—Cai and Wang (1998) examined several sources of CO<sub>2</sub> in the Satilla River estuary and concluded that pelagic respiration in estuarine water, simple mixing of acidic river water with seawater, and photodegradation of humic materials in estuarine surface waters were not sufficient to support the observed CO<sub>2</sub> flux. An important CO<sub>2</sub> source from the intertidal marshes and/or groundwater was therefore hypothesized. In this paper, we now include an examination of O<sub>2</sub> fluxes and an expanded CO<sub>2</sub> database, and we examine whether measured pelagic and benthic respiration rates can sustain both O<sub>2</sub> and CO<sub>2</sub> fluxes in longitudinal segments along the estuary.

Respiratory rates in waters throughout the Satilla River estuary (and the other four Georgia estuaries) are very similar, with day–night variations almost as great as seasonal variations and no clear difference between high and low salinities. Measurements of respiratory rates in the vicinity of Sapelo Island some 40 yr ago showed essentially the same range (Ragotzkie 1959). Simple calculations show, however, that these consistent values for microbial respiratory rates in estuarine water cannot produce the observed concentrations, and hence fluxes, of O<sub>2</sub> and CO<sub>2</sub>, in the low-salinity zones of the estuaries. Assuming that O<sub>2</sub> consumed by pelagic microbial communities in the estuaries is supplied from the atmosphere, the flux from the atmosphere (Eq. 1) must equal the depth-integrated pelagic O<sub>2</sub> consumption. If O<sub>2</sub> undersaturation is 50% in the low-salinity zone (Fig. 2a), the air-to-water flux is

$$\begin{aligned}
 &= K_T K_{O_2} [pO_2(\text{air}) - pO_2(\text{water})] \\
 &= 2.1 \text{ (m d}^{-1}) \cdot 1.1 \text{ (mol m}^{-3}\text{-atm)} \cdot [0.209 - 0.105] \text{ (atm)} \\
 &= 240 \text{ mmol m}^{-2} \text{ d}^{-1} \quad (\text{or } 88 \text{ mol m}^{-2} \text{ yr}^{-1}). \quad (3)
 \end{aligned}$$

Table 3. O<sub>2</sub> and CO<sub>2</sub> fluxes calculated from surface-water concentrations in the Satilla River estuary. All flux units are in 10<sup>9</sup> mmol d<sup>-1</sup> (per 10-km section of the estuary).

Distance from the mouth (km)	0–10	10–20	20–30	30–40	Total
River area (km <sup>2</sup> )	26.1	10.5	6.3	2.1	45.1
Estuarine O <sub>2</sub> flux	0.42	1.02	1.17	0.47	3.09
Estuarine CO <sub>2</sub> flux	0.42	0.34	1.13	0.47	2.36
Marsh area (km <sup>2</sup> )	37	48	67	25	177
Salt marsh O <sub>2</sub> consumption rate*	0.88	1.14	1.59	0.59	4.19

\* Calculated assuming 55 mmol O<sub>2</sub> m<sup>-2</sup> d<sup>-1</sup> (the average value from Table 2) for benthic consumption and 80 mmol m<sup>-3</sup> d<sup>-1</sup> (Pomeroy et al. 1972) for overlying water consumption, based on an average water depth of 0.5 m.

For the O<sub>2</sub> flux to be sustained by water-column respiration in the low-salinity regions of the estuary (given mean water depths for the Satilla = 3–4 m), respiratory rates of 80 and 60 mmol m<sup>-3</sup> d<sup>-1</sup> are required to balance O<sub>2</sub> flux for water depths of 3 and 4 m, respectively. The respiratory rates measured in the estuarine waters, however, are only 8–23 mmol m<sup>-3</sup> d<sup>-1</sup> (Table 1). Respiratory rates in water over the marsh at high tide are significantly higher than rates in the estuarine water, reported as 55, 78, and 113 mmol m<sup>-3</sup> d<sup>-1</sup> (Pomeroy et al. 1972; Table 2). Yet given average water depths of intertidal marshes at high tide of <0.5 m, these respiration rates are also much lower than those required to sustain the observed O<sub>2</sub> deficit. A large part of the respiratory O<sub>2</sub> consumption in low-salinity waters, therefore, is hypothesized to occur in the sediments of the estuary and marshes. Benthic flux measurements from the Sapelo Island and White Oak Creek intertidal marshes indeed indicate high benthic respiratory rates (about 30–80 mmol m<sup>-2</sup> d<sup>-1</sup>; Table 2). In a unit area sense, however, this flux is still much lower than the gas flux (~200 mmol m<sup>-2</sup> d<sup>-1</sup> at salinities of <10‰; Fig. 3). A mechanism will be presented below to explain how benthic marsh respiration can nonetheless support the large gas flux occurring over the estuarine surface.

In the high salinity zone of the Satilla estuary, in contrast, respiratory rates in the estuarine waters alone appear sufficient to support the calculated O<sub>2</sub> influx. With typical O<sub>2</sub> saturation levels of >90% in high-salinity waters (Fig. 2a), the O<sub>2</sub> flux is calculated as <60 mmol m<sup>-2</sup> d<sup>-1</sup>. Given an average depth of 4 m, a pelagic respiration rate of <15 mmol m<sup>-3</sup> d<sup>-1</sup>, well within our range of measurements, can support the calculated atmospheric flux.

An alternative approach to reconciling respiratory rates with O<sub>2</sub> influx and CO<sub>2</sub> efflux data is to sum the gas fluxes over the entire estuary and compare this with estimated whole-system marsh fluxes based on measured respiratory rates. Calculated fluxes of CO<sub>2</sub> and O<sub>2</sub> along the Satilla estuary (Fig. 3) were integrated for every 10-km section based on the surface area of each section (Table 3). We then calculated the oxygen consumption in the intertidal marshes for each section based on the area of the marsh (which is much larger than the surface area of the estuary; Table 3), assuming 6 h d<sup>-1</sup> of tidal inundation to a depth of 0.5 m. The rate of benthic respiration during inundation was assumed to be 55 mmol m<sup>-2</sup> d<sup>-1</sup> (the average value from Table 2), and the rate of overlying water respiration was assumed to be 80 mmol m<sup>-3</sup> d<sup>-1</sup> (based on the median value measured by Pomeroy et al. [1972] in marshes near Sapelo Island). For

each section individually and for the estuary as a whole, consumption of O<sub>2</sub> (and release of CO<sub>2</sub>) occurring from intertidal marsh sediments and in the overlying water during tidal inundation is sufficient to sustain the large gas transfer rates (Table 3). The above calculation demonstrates that the inclusion of respiration occurring over the extensive area of intertidal marsh is critical for balancing the low O<sub>2</sub> and high pCO<sub>2</sub> values and gas fluxes calculated for the estuary.

*A mass-balance model for the Satilla River estuary*—In the above section, we showed that for the Satilla estuary as a whole, it is necessary to consider respiration in the water and sediments of the intertidal marshes to support the calculated estuarine O<sub>2</sub> and CO<sub>2</sub> fluxes from the estuary. Here, we apply a more detailed mass-balance calculation to the individual 5-km sections of the estuary to determine whether a mass-balance approach can generate realistic profiles of O<sub>2</sub> and CO<sub>2</sub> partial pressures in surface waters of the estuary. This mass balance is based only on the estuarine water (including estuarine water flooding the marshes at high tide); direct gas exchanges between the atmosphere and marsh grasses and between the atmosphere and the marsh sediments during low tide are not included. Furthermore, we confine the model to summer months, the season for which our field data are most complete.

For the oxygen mass-balance model, we consider net benthic O<sub>2</sub> consumption while the marsh is flooded, net pelagic O<sub>2</sub> consumption in the flooding marsh water, benthic O<sub>2</sub> consumption in estuary bed sediments, pelagic O<sub>2</sub> consumption in estuarine water, and photosynthesis in estuarine water. We assume that net respiration is balanced by O<sub>2</sub> gas exchange with the atmosphere. The mass-balance formula is then constructed as follows: respiration in marsh sediments + respiration in marsh water + respiration in estuarine water + estuarine sediments – photosynthesis = estuary water-to-air flux + marsh water-to-air flux, or

$$\begin{aligned} & \frac{1}{4}F_m A_m + \frac{1}{4}R_m A_m H_m + R_r A_r H_r + F_r A_r - R_p A_r H_p \\ & = K_T^r K_{O_2} \Delta(pO_2)_r A_r + \frac{1}{4}K_T^m K_{O_2} \Delta(pO_2)_m A_m \end{aligned} \quad (4)$$

In Eq. 4,  $F$  represents benthic fluxes (in units of mmol m<sup>-2</sup> d<sup>-1</sup>), and  $R$  represents rates of respiration or photosynthesis (in units of mmol m<sup>-3</sup> d<sup>-1</sup>).  $A$  and  $H$  represent area (m<sup>2</sup>) and height (m), and super- and subscripts  $m$ ,  $r$ , and  $p$  indicate parameters for the marsh, river, or photosynthesis, respectively. We assume a 3-h inundation of water over the marsh-

es during each tide for a daily total of 6 h of inundation (i.e., one-quarter of a 24-h period).

Benthic O<sub>2</sub> fluxes measured in chamber incubations in the intertidal marsh have a large range of variation (Table 2). We therefore use two values for  $F_m$  in the model, which represent the highest and lowest rates measured (10 and 30 mol m<sup>-2</sup> yr<sup>-1</sup>, or 30 and 80 mmol m<sup>-2</sup> d<sup>-1</sup>).  $R_m$ , the rate of respiration in water overlying the marsh, is assumed to be 80 mmol m<sup>-3</sup> d<sup>-1</sup> (Pomeroy et al. 1972).  $R_r$ , the rate of respiration in estuarine water, is assumed to be 20 mmol m<sup>-3</sup> d<sup>-1</sup> based on the July 1997 cruise data.

Photosynthetic rates have not been measured extensively in the estuaries of Georgia. However, summer rates for the Duplin River (a tidal creek behind Sapelo Island) are about 130 mmol m<sup>-2</sup> d<sup>-1</sup> (Pomeroy et al. 1981). One approach to estimating photosynthetic rate would be to apply this rate to the estuary by correcting for the depth of light penetration in the estuary relative to the Duplin River. However, productivity is likely to be quite patchy in these systems, and light penetration depths may show significant spatial variability. Alternatively, Hopkinson (1985) estimated the ratio of primary production to respiration to be 0.72 for the Georgia nearshore, and Smith and Hollibaugh (1993) also estimate the average ratio of photosynthesis to respiration in estuaries worldwide to be 0.8–0.9. Therefore, we chose instead to estimate photosynthesis by assuming that: (1) together with flux from the air, primary production at the estuary mouth maintains a near saturation of O<sub>2</sub>, and (2) upstream from the estuary mouth, the rate of photosynthesis decreases according to the ratio of depth of the euphotic zone relative to the total depth. With this approach, production integrated over the entire estuary is approximately 75% of the respiration in estuarine water and sediments, and the ratio of photosynthesis to respiration is 0.97 at the river mouth. We use 0.5 m as the depth of the euphotic zone for water near the estuary mouth and 0.25 m for mid- to low-salinity regions (Sheldon and Moran unpubl. data). Although there are clearly large uncertainties in our estimate of the photosynthetic rate, the effects on predicted dissolved O<sub>2</sub> concentrations are rather small in the low-salinity zone. For example, at the 30-km estuary section, doubling the assumed euphotic zone from 0.25 to 0.5 m only increases the calculated O<sub>2</sub> saturation by 1.2%. (Here, percent change means relative change in the percent saturation, i.e., an increase from 50 to 51% is a 2% change.)

Another unknown term in the Satilla mass-balance model is oxygen consumption in the estuarine sediments. For modeling purposes, we assume a value equivalent to the lowest estimate of marsh benthic flux (30 mmol m<sup>-2</sup> d<sup>-1</sup>). Benthic O<sub>2</sub> flux is likely to vary among estuary sections in accordance with content of labile organic matter. However, since the ratio of estuarine sediments to marsh sediments is small, the uncertainty of this flux influences the final results only slightly. For example, at the 30-km estuary section, doubling the estuarine sediment O<sub>2</sub> flux only decreases predicted oxygen saturation by 0.7%.

There are no data available on gas exchange rate constants over intertidal marsh waters. The presence of vegetation in the marshes acts to decrease wind speed and water turbulence, and marsh waters are generally still. We have mea-

sured wind speeds of 0.05–0.2 m s<sup>-1</sup> at a height of 20 cm above the water surface (within the grass), compared to speeds of 1–2 m s<sup>-1</sup> at a height of 2 m above the water (above the grass) in the Satilla River marshes. Wind speeds over the open waters of the estuarine are higher. Thus, we expect the gas transfer velocity across the air–water interface to be significantly lower for the intertidal marshes than for the estuary (including the large creeks) and assume  $K_T^m$  equals one-third to one-half of  $K_T^r$ . The average O<sub>2</sub> saturation in intertidal marsh waters is lower than in estuarine water for an equivalent section of the estuary. However, because stratification is the typical condition in the marsh,  $\Delta pO_2$  across the air–water interface is actually smaller than for the estuary. We assume that  $\Delta pO_2$  for the marsh air–water interface equals one-third to one-half of  $\Delta pO_2$  for the estuary air–water interface. For the combined parameter of  $K_T^m \Delta pO_2$ , we therefore use a value approximately one-sixth of  $K_T^r \Delta pO_2$ . Since marshes are inundated only 6 h d<sup>-1</sup>, the contribution of marsh water–air fluxes to the model is relatively small. Again, at the 30-km estuary section, using a value of one-fourth (i.e., increasing our estimate of gas exchange over marsh water) or a value of one-eighth (i.e., decreasing our estimate) causes only a moderate increase of 5% or a decrease of 3%, respectively, in calculated O<sub>2</sub> saturation.

This mass-balance model is applied to each 5-km section of the Satilla River estuary from –5 to 50 km from the estuary mouth (Fig. 4a). Because the model has no hydrologic mixing mechanism, we average the model output of each section with its immediate upstream neighbor to obtain the final value. This is intended to smooth the model output and does not change the major features of the results.

A similar mass-balance model was also constructed for CO<sub>2</sub> fluxes (Fig. 4b). All of the parameters were the same as those for the O<sub>2</sub> mass balance, assuming the Redfield ratio (138:106).

The main features of estuarine water O<sub>2</sub> saturation and  $pCO_2$  profiles are reproduced by the mass-balance models. These are: (1) low dissolved O<sub>2</sub> concentrations (~50% saturation) in low-salinity waters (<15‰ and 20 km upstream from the estuary mouth), (2) near saturation of O<sub>2</sub> in high-salinity waters, and (3) high  $pCO_2$  values (>4,000  $\mu$ atm) in low-salinity waters.

The most critical factor in the mass-balance models that creates the very low O<sub>2</sub> concentrations and the very high  $pCO_2$  values in low-salinity estuarine water is the ratio of marsh area to estuary area. This ratio reflects the fact that the marsh waters are funneled into the estuary during low tide, focusing the respiratory signals that have accumulated during high tide (due to less efficient gas exchange over the vegetated marsh surface) into a smaller (but deeper) estuary. Thus, the respiration in the marshes establishes an O<sub>2</sub> deficit and CO<sub>2</sub> excess that can subsequently support a large gas flux over the estuary surface. A conceptual model of this view is presented in Fig. 5. The ratio of marsh area to estuary area, referred to here as the estuarine focusing factor (EFF), is >5 upstream of 20 km (Fig. 6), where O<sub>2</sub> saturations are typically <65% and  $pCO_2$  values are >3,000  $\mu$ atm. Net areal integrated respiration rates in the Satilla estuarine–intertidal complex peak at  $13 \times 10^8$  mmol d<sup>-1</sup> in the 25–30-km section (Fig. 6), the same section of the estuary where

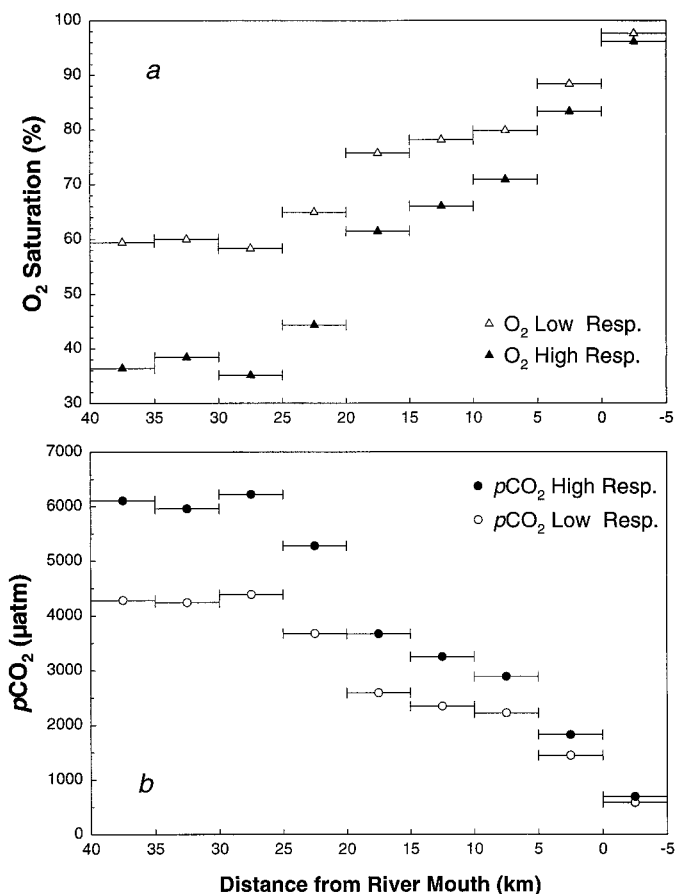


Fig. 4. Predicted dissolved  $O_2$  concentrations (a) and  $pCO_2$  values (b) vs. river distance for the Satilla River estuary based on the mass-balance model output. The models were run assuming benthic respiratory rates in the low range of measured values ( $27 \text{ mmol } O_2 \text{ m}^{-2} \text{ d}^{-1}$  or  $54 \text{ mmol C m}^{-2} \text{ d}^{-1}$ ) and in the high range ( $80 \text{ mmol } O_2 \text{ m}^{-2} \text{ d}^{-1}$  or  $120 \text{ mmol C m}^{-2} \text{ d}^{-1}$ ).

the EFF peaks (EFF = 15). Net respiration decreases both upstream and downstream from this point, in parallel with the decrease in intertidal marsh area. The generally higher EFF in the low-salinity region of the Satilla corresponds with concentrated marsh signals (i.e., low  $O_2$  saturation and high  $pCO_2$  values). Seaward of 20 km, although the net respiration rate is still high, the larger estuarine area keeps the EFF low, resulting in a diluted marsh signal (i.e., a low respiration signal and near equilibrium  $O_2$  and  $pCO_2$  concentrations).

Our model is based on a mass-balance approach but has no mixing mechanism among boxes. The model assumes that  $O_2$  consumption within the estuarine system is compensated by  $O_2$  flux from the atmosphere, with no net flux of  $O_2$  to or from a "box." Given this assumption, the model generates  $O_2$  concentrations (or  $pCO_2$  values) for the end members, just as it does for internal sections, by reference to atmospheric gas concentrations through the gas diffusion law. This simple approach allows us to investigate the biogeochemical mechanisms controlling the observed concentrations, including the low  $O_2$  concentrations consistently observed in low-salinity regions of the estuary. There are,

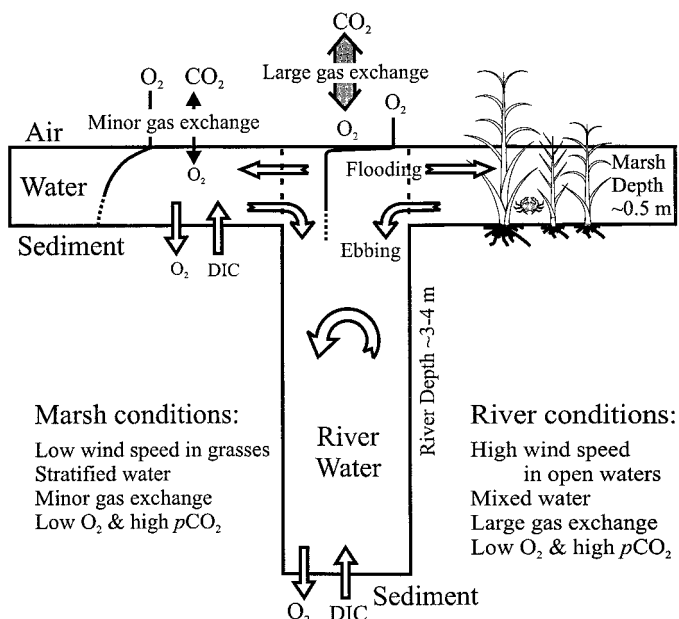


Fig. 5. A conceptual model of gas exchange in the estuary. This vertical profile shows the focusing of respiration signals from a large area of intertidal marsh (where environmental conditions support low gas exchange rates) into a much smaller surface area of the estuary (where conditions support large gas exchange rates). Expected  $O_2$  concentration profiles are also presented for river and marsh waters, respectively.

however, significant limitations to an approach that does not consider estuarine hydrodynamics. For example, because river flows are not considered in the model, it is not possible to examine the influence of seasonal or episodic changes in freshwater flow on the magnitude of intertidal marsh influence on estuarine gas exchange.

*The role of intertidal marshes in other Georgia estuaries*—Extensive intertidal marshes are characteristic of the coastal zone of the southeastern U.S. Based on the results of the Satilla mass-balance model, we hypothesized that the EFF concept could be used to predict the extent of marsh influence on the concentrations of  $O_2$  and  $CO_2$  in other southeastern estuaries. Mass-balance analyses were therefore applied to the four other Georgia estuaries.

The St. Marys River, which, like the Satilla, is confined exclusively to the coastal plain province, is very similar to the Satilla in EFF patterns (Fig. 7b) and predicted  $O_2$  saturation patterns (Fig. 7a). The two piedmont rivers, the Altamaha and the Savannah, have much lower EFFs, and the predicted estuarine  $O_2$  concentrations are close to saturation (Fig. 7a,b). The Ogeechee is intermediate for both of these characteristics. When  $O_2$  distributions predicted by the mass-balance models are compared to empirical dissolved  $O_2$  data from the estuaries, it is evident that the mass-balance models generate realistic profiles of  $O_2$  concentrations in estuarine surface waters (Fig. 7a). Although the generated profiles for the Savannah and Altamaha Rivers show the greatest deviations from the empirical data (but not from the pattern of the empirical data), particularly in the midestuarine region,

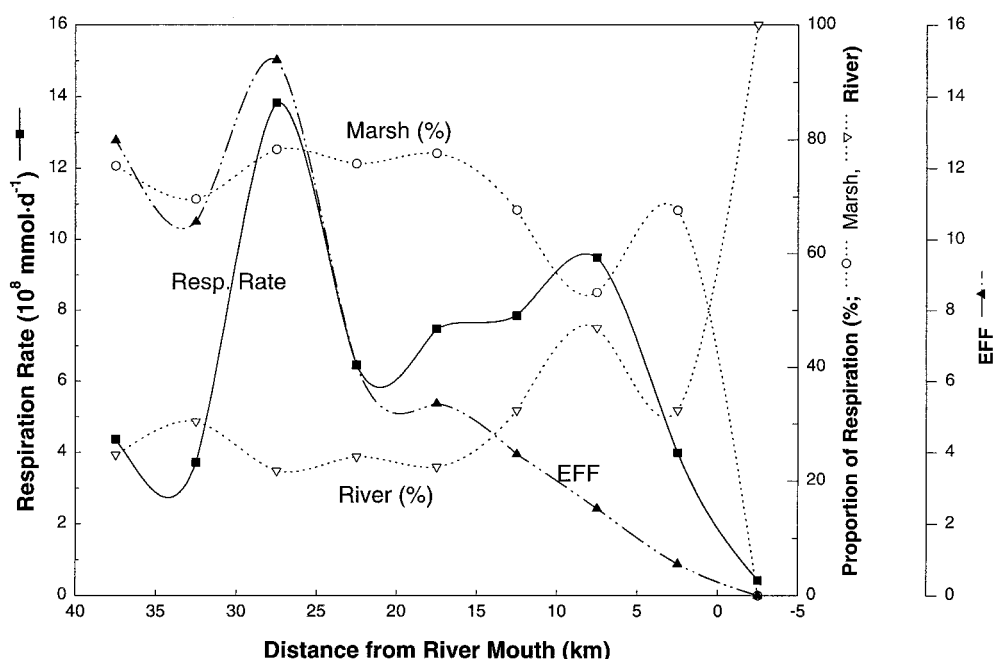


Fig. 6. The ratio of marsh area to estuary area (EFF), the respiration rate integrated over each 5-km section of the estuarine-marsh complex, and the proportion of total respiration attributable to intertidal marsh or estuary for the Satilla River.

this may be related to the fact that the models do not include exports from forested floodplains, managed rice impoundments (mostly Altamaha River), and other possible sources of respiratory products. Nonetheless, the magnitude of the EFF has an important influence on calculated O<sub>2</sub> concentrations, emphasizing the role of intertidal marsh respiration in determining gas flux from the estuaries.

*The role of anaerobic processes*—Sulfate reduction has been found to be an important mechanism for the degradation of organic matter in salt marsh ecosystems (Howarth and Teal 1980). Dissimilatory sulfate reduction rates of 150 mmol CO<sub>2</sub> m<sup>-2</sup> d<sup>-1</sup> (Skyring et al. 1979) and 60–180 mmol CO<sub>2</sub> m<sup>-2</sup> d<sup>-1</sup> (Howarth and Giblin 1983) have been measured previously in Georgia marshes, and these rates are comparable to the total DIC fluxes measured by benthic chamber incubations in this study (50–120 mmol C m<sup>-2</sup> d<sup>-1</sup>; Table 2). As discussed by Howarth (1984) and King et al. (1982, 1985), sulfate reduction generally accounts for 25–70% of the total respiration in nearshore sediments and 70–90% in high-salinity marsh sediments. Nonconservative alkalinity increases in sediment-dominated aquatic systems, such as was observed in the Satilla River (October 1995) (Cai and Wang 1998) and in White Oak Creek (July 1997; Cai unpubl. data), have commonly been attributed to sulfate reduction (Bernier et al. 1970; Bernier 1978; Smith and Hollibaugh 1997).

Although potentially quite large, the carbon flux mediated by sulfate reduction is not likely to be problematic for our mass-balance models. During aerobic respiration, the ratio of O<sub>2</sub> consumption to DIC and NH<sub>3</sub> production is 106:106:16. To nitrify the NH<sub>3</sub>, an additional 32 mol of O<sub>2</sub> is consumed. During anaerobic respiration dominated by sulfate

reduction, the ratio of DIC production to H<sub>2</sub>S and NH<sub>3</sub> production is 106:53:16. To oxidize the H<sub>2</sub>S, 106 mol of O<sub>2</sub> is required, and to nitrify the NH<sub>3</sub>, 32 mol of O<sub>2</sub> is required. Therefore, if the H<sub>2</sub>S and NH<sub>3</sub> produced from anaerobic respiration diffuse into the oxic zone and are oxidized to SO<sub>4</sub> and NO<sub>3</sub>, there is no difference in O<sub>2</sub> consumption between oxic respiration and anaerobic sulfate reduction followed by reoxidation of reduced products (138 mol of O<sub>2</sub> in each case), much as has been noted for subtidal sediments (Canfield et al. 1993). However, if a significant amount of sulfide were buried in the sediments or escaped to the atmosphere, then DIC production would be significantly higher than O<sub>2</sub> consumption. A clear alkalinity signal would also be measured, as was the case in Tomales Bay (Smith and Hollibaugh 1997). The larger DIC flux relative to oxygen flux measured with the same incubation chamber (although on subsequent days) in this study (Table 2) might therefore reflect sulfide burial. However, the buried sulfide could be re-oxidized seasonally (Howarth and Giblin 1983). Carbon loss from the marshes as methane was previously found to be on the order of 5 mmol m<sup>-2</sup> d<sup>-1</sup> (King and Wiebe 1978) and is therefore much smaller than DIC production.

*The estuarine outwelling hypothesis revisited*—Our mass-balance approach indicates that the bulk of respiratory activity in the estuary-intertidal marsh complex occurs in the marsh sediments and overlying water. Respiratory rates in estuarine water are not high (Table 1) and may well be limited by the availability of labile carbon. This analysis does not support the hypothesis of a major transfer of labile organic carbon from the salt marshes to estuaries.

In earlier work in the Georgia estuarine-intertidal marsh complex, Chalmers et al. (1985) likewise did not observe

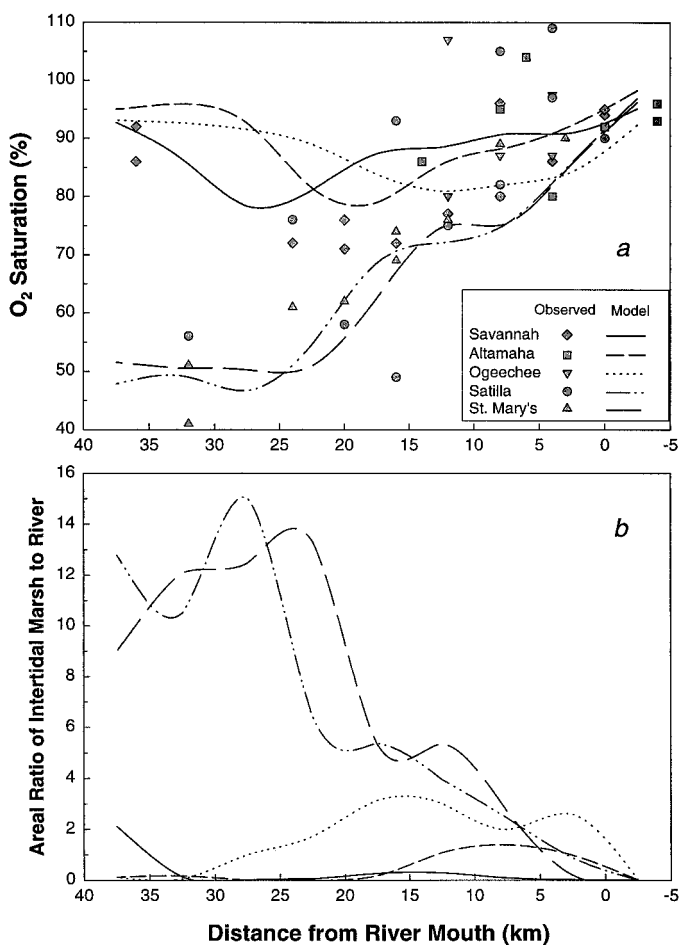


Fig. 7.  $O_2$  mass-balance model output (a) and EFF (b) vs. distance for five Georgia estuaries.

the export of organic carbon from salt marshes but instead, predicted an annual accumulation of  $30 \text{ mol m}^{-2} \text{ yr}^{-1}$ . Although it was hypothesized that most of the excess organic carbon was removed by respiration or emigration of motile organisms, this possibility remained largely untested. Our mass-balance model of the Satilla, however, can be used to estimate the magnitude of respiratory losses from intertidal marshes. The model predicts  $CO_2$  losses from the estuarine-marsh system during tidal flooding of  $1.8\text{--}2.7 \times 10^9 \text{ mol C yr}^{-1}$ . When the intertidal marshes are not flooded, we estimate additional respiratory losses of  $2.5 \times 10^9 \text{ mol C yr}^{-1}$ , based on  $CO_2$  flux measurements of  $18.7 \text{ mol m}^{-2} \text{ yr}^{-1}$  (Pomeroy 1959), an intertidal marsh area of  $177 \times 10^6 \text{ m}^2$  in the Satilla system, and 18 h of nonflooded conditions per day. Thus, the total C leaving the Satilla estuarine-marsh complex as  $CO_2$  is estimated at  $4.3\text{--}5.3 \times 10^9 \text{ mol C yr}^{-1}$  (or  $24\text{--}30 \text{ mol C m}^{-2} \text{ yr}^{-1}$ ), a value very close to the organic C "accumulation" rate of Chalmers et al. (1985) ( $5.3 \times 10^9 \text{ mol yr}^{-1} = 30 \text{ mol m}^{-2} \text{ yr}^{-1} \cdot 177 \times 10^6 \text{ m}^2$ ). This calculation indicates that most of the organic C unaccounted for by Chalmers et al. (1985) could be leaving the marsh as respired  $CO_2$  and argues that the likelihood of substantial organic carbon exports from the marsh is low, at least by comparison to the inorganic carbon exports.

Although fluxes of  $O_2$  and DIC from the intertidal marshes to the estuary are estimated to be quite large, dynamic cycling between the water and atmosphere results in rapid exchanges of the dissolved gases. As a result, the flux of DIC from the estuaries to the nearshore ocean is predicted to be comparatively small, with only a small signal from intertidal marsh respiratory activity evident in the coastal ocean.

**Potential significance for global  $CO_2$  balances**—Our analysis of the Georgia estuarine systems indicates that a large fraction of the  $CO_2$  fixed in the salt marshes is respired there and thus, that the net flux of  $CO_2$  to or from the atmosphere must be small. Despite a small net flux, however, the gross flux of  $CO_2$  in these intertidal systems is very large, suggesting the possibility that seasonal phase shifts in the periods of peak production and respiration might be of importance on a global or regional scale. For example, the total global (maritime) salt marsh area is estimated to be  $3.8 \times 10^7 \text{ ha}$  (Stuedler and Peterson 1984). Considering estuarine water marshes as well, which in the Georgia estuaries are equivalent to the area of the salt marshes (Chalmers pers. comm.), a reasonable estimate of the global area of intertidal (maritime plus estuarine) marshes is  $7.6 \times 10^7 \text{ ha}$ . The  $CO_2$  respired annually from these marshes can be estimated at approximately  $18\text{--}23 \times 10^{12} \text{ mol yr}^{-1}$  (i.e.,  $7.6 \times 10^7 \text{ ha} \cdot 24\text{--}30 \text{ mol m}^{-2} \text{ yr}^{-1}$ ). By comparison, the riverine DIC delivered to the world oceans annually is approximately  $35 \times 10^{12} \text{ mol C yr}^{-1}$  (Garrels and Mackenzie 1972); the net  $CO_2$  release from the coastal oceans worldwide is  $7 \times 10^{12} \text{ mol C yr}^{-1}$  (Smith and Hollibaugh 1993); and the total terrigenous organic C delivery to the ocean is  $34 \times 10^{12} \text{ mol C yr}^{-1}$  (Smith and Hollibaugh 1993). Thus, extrapolating from the estuarine-intertidal marsh systems of the southeastern U.S., a seasonal imbalance in  $CO_2$  uptake and release, attributable to a phase lag between production and respiration, is of sufficient magnitude to be an important factor in global  $CO_2$  models that incorporate seasonal change.

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