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Transport of dissolved inorganic carbon from a tidal freshwater marsh to the York River estuary

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Abstract

The cycling of dissolved inorganic carbon (DIC) and the role of tidal marshes in estuarine DIC dynamics were studied in a Virginia tidal freshwater marsh and adjacent estuary. DIC was measured over diurnal cycles in different seasons in a marsh tidal creek and at the junction of the creek with the adjacent Pamunkey River. In the creek, DIC concentrations around high tide were controlled by the same processes affecting whole-estuary DIC gradients. Near low tide, DIC concentrations were 1.5–5-fold enriched relative to high tide concentrations, indicating an input of DIC from the marsh. Similar patterns (although dampened in magnitude) were observed at the creek mouth and indicated that DIC was exported from the marsh. Marsh pore-water DIC concentrations were up to 5 mmol L^{-1} greater than those in the creek and suggested a significant input of sediment pore water to the creek. A model of tidal marsh DIC export showed that, on a seasonal basis, DIC export rates were influenced by water temperature. The composition of exported DIC averaged 19% dissolved CO_2 and 81% HCO_3^- and CO_3^{2-}. Although CO_2 can be lost to the atmosphere during transit through the estuary, DIC in the form of carbonate alkalinity is subject to export from the estuary to the coastal ocean. When extrapolated to an estuarywide scale, the export of marsh-derived DIC to the York River estuary explained a significant portion (47 ± 23%) of excess DIC production (i.e., DIC in excess of that expected from conservative mixing between seawater and freshwater and equilibrium with the atmosphere) in this system. Therefore, CO_2 supersaturation, by itself, does not indicate that an estuary is net heterotrophic.

One approach to understanding the cycling of organic carbon within ecosystems is through measurements of total system metabolism, given that the production and removal of organic matter are intimately linked to total dissolved inorganic carbon (DIC, or ΣCO_2) and O_2 cycling. Recent studies of estuarine CO_2 and DIC dynamics have shown that estuaries are generally supersaturated with respect to CO_2 and exhibit high rates of net heterotrophy (i.e., respiration > photosynthesis; Smith and Hollibaugh 1993; Frankignoulle et al. 1998; Gatusso et al. 1998), although the main stem of Chesapeake Bay is net autotrophic (Kemp et al. 1997). Sources of CO_2 and DIC to estuarine waters include water-column and benthic respiration, riverine and groundwater inputs, photodegradation of dissolved organic matter, and inputs from intertidal marshes (Hopkinson and Vallino 1995; Kemp et al. 1997; Cai and Wang 1998). Accurate quantification of rates of net heterotrophy requires that one account for DIC produced within the estuary through in situ organic matter decomposition as well as DIC produced in the watershed (e.g., in intertidal wetlands or groundwater) and subsequently transported into the estuary. Thus, CO_2 supersaturation, by itself, is insufficient evidence for declaring the trophic status (net autotrophy or heterotrophy) of an estuary or other open ecosystem. Although the total area of estuaries is globally small, the biogeochemical cycling of carbon in these systems may be regionally significant (e.g., Smith and Hollibaugh 1993; Frankignoulle et al. 1998), so a more robust understanding of the sources, cycling, and fates of DIC in estuarine waters is required.

Over the past 40 yr, the fluxes of particulate and dissolved organic carbon (POC and DOC) and inorganic nutrients between intertidal marshes and estuarine waters have been studied, primarily to determine whether the export of these materials could explain high rates of primary and secondary production in estuarine waters (Nixon 1980; Childers 1994; Dame 1994). Although there is no consensus on the magnitude or direction of marsh-estuary organic carbon fluxes, the export of DOC and POC from marshes followed by remineralization within the estuary is one mechanism that could explain high estuarine DIC concentrations. Additionally, there is potential for DIC transport from intertidal marshes to the estuary. However, there are few reports of this direct export of marsh-produced DIC (e.g., Cai and Wang 1998; Cai et al. 1999). The DIC may be added to waters overlying the marsh from plant decomposition, sediment metabolism, and the upward diffusion of marsh pore water. Potential inputs when the marsh surface is exposed to air include drainage of marsh pore water into tidal creeks and DIC fluxes from subtidal creek sediments. To accurately quantify the total DIC transport from a marsh, all routes of export must be considered.

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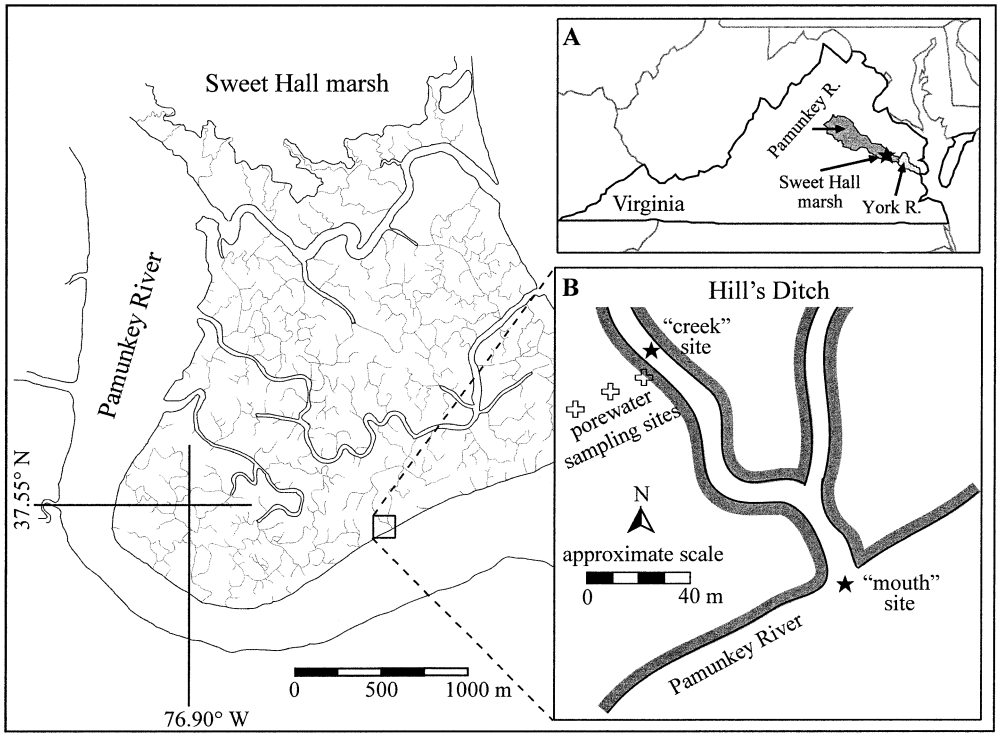

Fig. 1. Map of Sweet Hall marsh, Virginia. Fine gray lines indicate tidal creeks used in calculations of total marsh DIC export (see text for details). Insets show the location of (A) York and Pamunkey River watersheds and Sweet Hall marsh in Virginia and (B) creek and mouth water sampling sites and pore-water sippers within the marsh. Creek width exaggerated on inset for clarity (actual creek width, ~4 m).

Several recent studies have suggested that there must be a significant marsh source of DIC to estuarine waters to account for measured levels of CO_2 supersaturation (Cai and Wang 1998; Cai et al. 1999; Raymond et al. 2000). The major objectives of the present study were to determine whether DIC is exported from intertidal marshes, identify possible sources of this DIC, and quantify this export in relation to whole-estuary DIC dynamics. Hourly measurements of DIC were made over diurnal cycles in an intertidal creek draining a tidal freshwater marsh in Virginia. Simultaneous measurements were made at the mouth of the tidal creek to determine whether DIC added to the creek was subsequently exported to the adjacent river. Marsh pore-water DIC was measured to determine whether drainage of pore water into the creek could explain the observed temporal patterns in creek DIC concentrations. To determine seasonal differences in marsh DIC cycling, data were collected during the period of maximum marsh macrophyte biomass (June), in late summer, when rates of senescence and decomposition were high (August), and in November, when rates of plant productivity and marsh respiration were low. The observed tidal and seasonal changes in DIC were combined with estimates of tidal water transport through marsh creeks, to quantify the annual export of DIC from the marsh and understand the significance of tidal marshes to the DIC budget of the adjacent estuary. In this article, we have defined the landward edge of the estuary as the boundary between subtidal waters and intertidal marshes (or nontidal uplands).

Materials and methods

Study site—Sweet Hall marsh (Fig. 1) is a 401-ha tidal freshwater marsh located on the Pamunkey River, ~69 km (by river) from the mouth of the York River, Virginia. The marsh is a site within the Chesapeake Bay National Estuarine Research Reserve system in Virginia (CB-NERRVA) and is seasonally dominated by the macrophytes *Peltandra virginica, Pontederia cordata,* and *Zizania aquatica.* Sweet Hall has been the site of previous studies of marsh carbon cycling, including measurements of total community photosynthesis and respiration (Neubauer et al. 2000) and sediment deposition and accretion (Neubauer et al. 2002). Most of Sweet Hall marsh (including our study site) is isolated from the mainland by the Pamunkey River and a relatively deep tidal channel (>2 m), so the marsh does not receive direct groundwater inputs from a shallow aquifer. At Sweet Hall, the Pamunkey River is microtidal with a tidal range of 90 cm during spring tides. Historical records indicate that the long-term average salinity at Sweet Hall was 0.5 (Brooks 1983). However, during the year of our study (1999), salinity ranged from 0 to 15.9 (average 2.8; CB-NERRVA unpublished data), with the highest salinities in late August and early September after a dry summer. Pamunkey River discharge rates during May to August 1999 were the lowest recorded over the past 30 years (USGS 2000).

Diurnal tidal sampling—Studies examining tidal exchanges of DIC among the marsh, creek, and river were

conducted on 29–30 June, 24–25 August, and 09–10 November 1999. All sampling dates were within 2 d of spring tide. Water samples were collected from a small tidal creek (Hill's Ditch) draining Sweet Hall marsh (hereafter referred to as the ''creek'' site) and at the junction of this creek with the Pamunkey River (''mouth'' site; Fig. 1). Fifty-milliliter water samples were collected hourly using polypropylene syringes and immediately filtered for DIC analyses as described below. A YSI 6000 datasonde recorded water depth, salinity, pH, temperature, and dissolved oxygen (DO) at 15-min intervals. At the creek site, the water intake and YSI datasonde were located 10–15 cm above the creek bed. The intake at the mouth site was suspended from a floating platform and sampled 20–30 cm below the water surface (~5–70 cm above the sediment surface, depending on tidal stage).

Water samples for DIC analysis were filtered (0.45 μm Gelman Supor Acrodiscs) into 12.8-ml gas-tight Hungate tubes, stored on ice in the field and refrigerated until analysis. Sample DIC analyses were performed within 2 d of collection. Laboratory experiments with a range of DIC standards (0.5–7.0 mmol L^{-1}) showed no significant concentration changes over 12 d (data not shown). Fifty-microliter samples were injected into a vessel filled with 25 ml of 0.05 mol L^{-1} H_2SO_4 that was continuously sparged with CO_2-free N_2 into a LI-COR 6252 infrared gas analyzer. Calibrations were performed routinely by injecting a series of Na_2CO_3 standards (0.5–10 mmol L^{-1}). The median sample precision for 3–5 replicate standard injections was 0.01 mmol L^{-1}.

Pore-water sampling—Marsh pore water was sampled on the same dates as the creek and mouth water-column sites. Clusters of three pore-water samplers (''sippers'') were located at 1, 15, and 30 m along a transect extending from the creek bank (0 m) toward the marsh interior (30 m; Fig. 1). Each sipper had a 5-cm sampling window of porous sintered plastic (Porex) centered at a depth of 5, 15, or 25 cm. Prior to sampling, sippers were purged of water and filled with argon gas to maintain anaerobic conditions. Each sipper was then evacuated to a vacuum of 50–60 cm Hg and allowed to refill for 4–5 h before sampling. Water was collected from sippers within 1 h of low tide using polypropylene syringes and filtered for DIC analysis as described above. In spite of the relatively high vacuum and long recharge times, there were occasions when there was not enough water for DIC analyses.

DIC export calculations—To quantify the export of DIC from Sweet Hall marsh and place our data in a larger ecological context, we extrapolated DIC profiles from a single tidal creek to an estimate of whole marsh DIC flux to the subtidal estuary. In the absence of marsh DIC input or removal terms, the concentration of DIC in a marsh tidal creek will equal that in the adjacent river ($DIC_{creek} = DIC_{river}$). For this system, DIC_{river} was estimated using DIC versus salinity regressions for the York and Pamunkey Rivers (Raymond et al. 2000). Because of tidal changes in salinity, the calculated DIC_{river} concentrations varied by 0.1–0.2 mmol L^{-1} over the tidal cycle. For each hourly sampling point, the DIC enrichment due to marsh input (DIC_{marsh}) was calculated as the difference between measured (DIC_{creek}) and predicted (DIC_{river}) concentrations. The DIC_{marsh} term includes all DIC added within the marsh–tidal creek system. Periodically, DIC_{creek} was less than calculated DIC_{river} (generally by <0.05 mmol L^{-1}); on these occasions, we assumed that DIC_{marsh} was zero and within the prediction error of the DIC versus salinity regressions.

At Sweet Hall, water is confined to the tidal creeks at low tide, but the entire marsh is typically flooded to a depth of 20–40 cm at high tide. Seasonally, we determined when flooding of the marsh surface began (i.e., ''creek-full'' depth, D_{full}). To account for spatial variations in marsh elevation and temporal changes in tidal range (e.g., over spring-neap tidal cycles), we varied this depth by ± 10 cm to calculate a range of DIC export. Using a computer graphics package (Canvas 5.0; Deneba Systems), the total length of all creeks on a digitized USGS topographic map of Sweet Hall marsh was estimated as 48 km. Several deep (>2 m) and broad (>30 m) tidal channels that bisect the marsh were not included in this estimate. On the basis of the resolution of an individual pixel on the digitized map (4 × 4 m), we assumed that all creeks were 4 m wide. When water depth was below the creek-full depth ($D_{meas} < D_{full}$), the total volume of water in all tidal creeks at Sweet Hall was calculated using measured water depths and estimates of creek width and length. Thus, $V = [D_{meas} \times L \times W]$ where V is water volume (m^3), D_{meas} is measured water depth (m), L is total length of all creeks in the marsh (4.8×10^4 m), and W is creek width (4 m). When measured water depth was greater than the creek-full depth, the total volume of water in the marsh was calculated as the sum of water in the marsh creeks and that overlying the marsh. Thus, if $D_{meas} > D_{full}$, $V = [D_{full} \times L \times W] + [(D_{meas} - D_{full}) \times A]$ where A is the total area of Sweet Hall marsh (4×10^6 m^2; Silberhorn and Zacherle 1987).

Rates of DIC export were calculated during ebb tide when there was a hydrological export of water, and therefore DIC, from the marsh. This analysis only considers the transport of marsh-derived DIC (DIC_{marsh}). Thus, if there is no DIC enrichment (i.e., $DIC_{creek} = DIC_{river}$), the calculated DIC export rate will be zero. For each set of adjacent hourly time points during ebb tide ($t_{(i)}$ and $t_{(i+1)}$), the average DIC enrichment (DIC_{marsh}; mmol L^{-1}) was multiplied by the change in volume (V, in liters) to calculate hourly DIC export (DIC_{export}; mmol h^{-1}):

$$DIC_{export} = [(DIC_{marsh,t(i)} + DIC_{marsh,t(i+1)})/2] \times (V_{t(i)} - V_{t(i+1)})$$

Marsh DIC fluxes were summed over two ebb tides per day and divided by the total area of Sweet Hall marsh to calculate the average flux per m^2 of marsh per day for each sampling date.

The evasion of CO_2 from marsh waters to the atmosphere was calculated using the gas-exchange coefficient (k) and the CO_2 concentration gradient (under the assumption of an atmospheric CO_2 concentration of 360 ppmv) across the air-water interface as flux $= k \times ([CO_2]_{water} - [CO_2]_{air})$. The CO_2 concentrations were calculated using measured DIC, salinity, temperature, and pH data (Park 1969; Weiss 1974; Millero 1995). Additionally, we used DIC concentrations from Raymond et al.'s (2000) DIC versus salinity regressions to estimate the amount of CO_2 contributed by river water

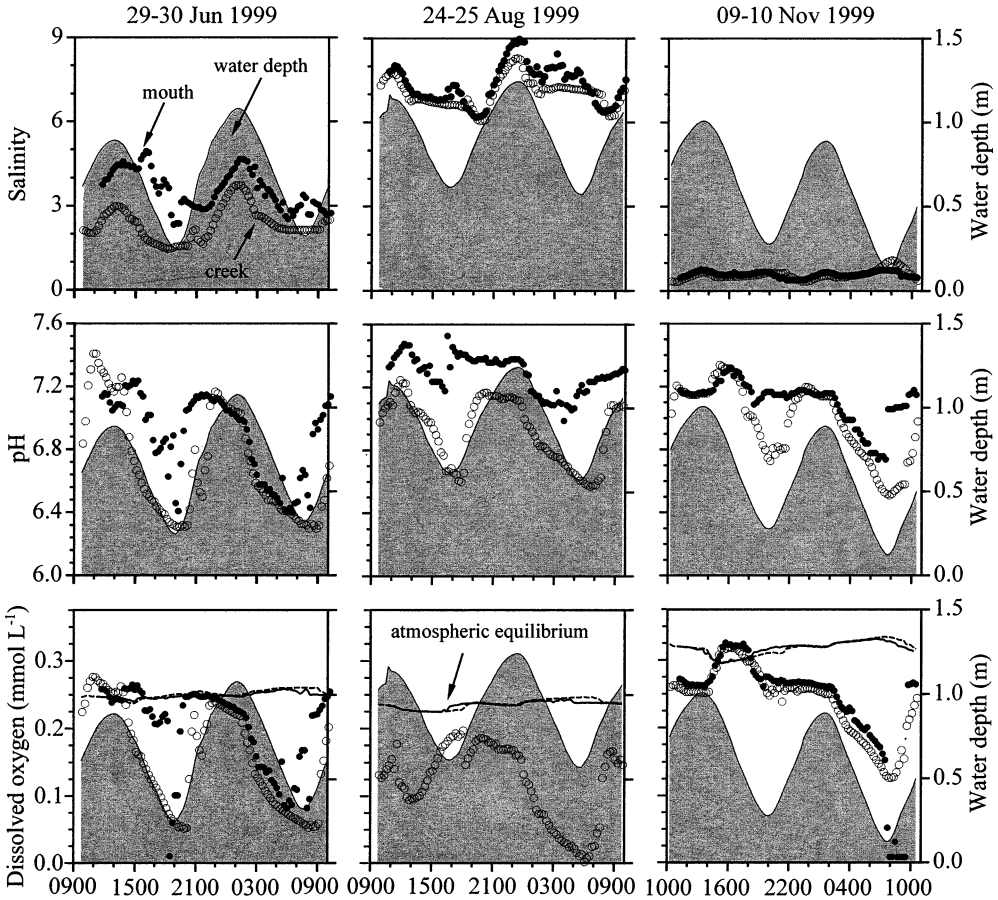

Fig. 2. Water column conditions at the creek and mouth sites. Open circles are from the creek site; closed circles are from the creek mouth. Gray shading on all panels indicates creek water depth. Dashed and solid lines in the DO panels indicate the expected concentration at atmospheric equilibrium for the creek and mouth sites, respectively. The dissolved oxygen sensor at the mouth site malfunctioned in Aug 1999. All times are EST.

that flooded the marsh. The difference between the dissolved CO_2 concentrations calculated from our data and those derived from the data of Raymond et al. (2000) represented CO_2 added by the marsh and associated tidal creeks. We used the average k value of 4.7 cm h^{-1} reported by Raymond et al. (2000) for the York and Pamunkey River estuaries as our upper limit for k. Because the gas-exchange coefficient in the marsh may be 33%–50% of this value because of the sheltering effects of marsh vegetation (Cai et al. 1999), 1.6 and 2.4 cm h^{-1} were used as additional estimates of k. Evasion rates (mmol C m^{-2} water h^{-1}) of total CO_2 and marsh-derived CO_2 were calculated hourly for each date when samples were collected. Whole-marsh fluxes were determined by multiplying the evasion rate (mmol C m^{-2} water h^{-1}) by the area of marsh flooded at each time point. Hourly evasion rates (mmol C h^{-1}) were summed and divided by the total area of Sweet Hall marsh to express CO_2 evasion as mmol C m^{-2} marsh d^{-1}.

Results and discussion

Water column conditions—During the sampling dates, the tidal range in the marsh creek varied between 0.55 (Aug) and 0.83 (Jun) m (Fig. 2). Water column temperatures were similar in June (23.8–28.8°C) and August (24.5–30.7°C) and lower in November (12.1–18.4°C). There were no significant differences in water temperature between the creek and mouth sites. There was a wide variation in salinity among sampling dates (Jun, 1.5–4.9; Aug, 6.1–8.9; and Nov, 0.3–1.1) as well as over individual tidal cycles (Fig. 2). Because salinity affects rates of alkalinity-generating processes such as sulfate reduction, these changes in salinity can affect the dynamics of marsh DIC cycling. Water column pH and DO followed similar tidal patterns, with lowest pH and DO concentrations near low tide (Fig. 2). The pH at the creek site was generally lower than at the mouth site, which suggests an input of more acidic water within the marsh-creek system. Measured DO concentrations were typically below atmospheric equilibrium but generally were not indicative of hypoxic or anoxic conditions.

Water column DIC concentrations—Within the water column, there were large variations in DIC concentrations over tidal and seasonal timescales (Fig. 3). Near high tides, DIC concentrations were similar at both creek and mouth sites (Jun, ~0.5 mmol L^{-1}; Aug, ~1.1 mmol L^{-1}; and Nov, ~0.5

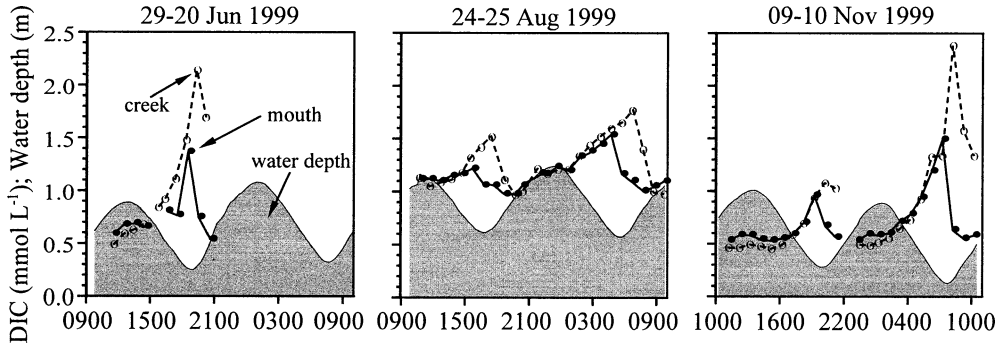

Fig. 3. Diurnal DIC profiles. Open circles are from the creek site; closed circles are from the creek mouth. Gray shading indicates creek water depth. Sampling in June 1999 was cut short due to severe weather. All times are EST.

mmol L^{-1}). These high-tide concentrations were within ± 0.05 mmol L^{-1} of those calculated from DIC versus salinity regression equations for the York and Pamunkey Rivers (Raymond et al. 2000; exception: one point in August was overestimated by 0.10 mmol L^{-1}). This suggests that the processes that affect estuarine DIC gradients in the York and Pamunkey Rivers also control high-tide DIC concentrations in the marsh tidal creek.

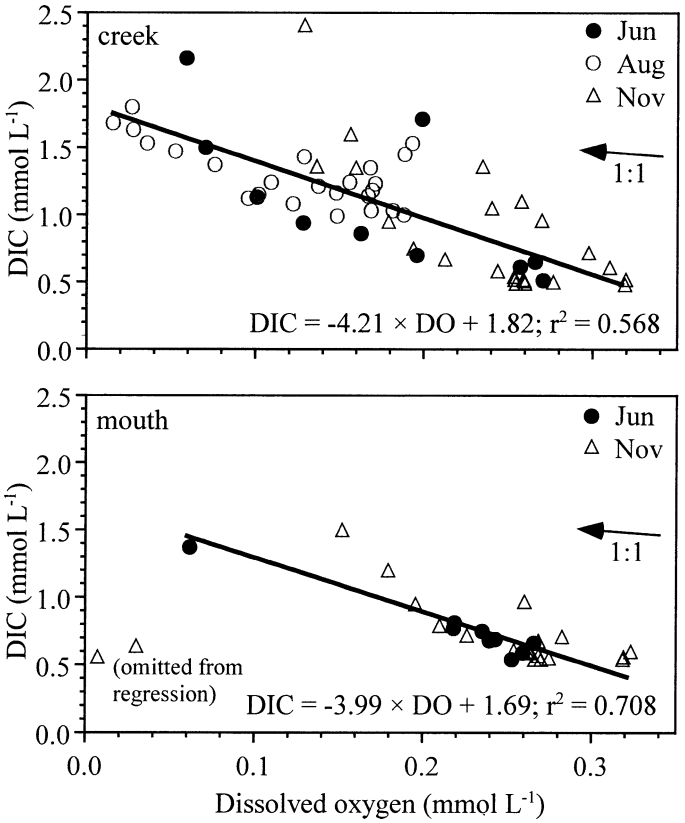

Fig. 4. Water column DIC vs. DO at the creek and mouth sites. Regression line for creek samples is fit through all data points; the line for mouth samples is fit through all points except the two low DO, low DIC outliers from November. These outliers were omitted from the regression analysis because we suspect that the DO sensor was in the sediments rather than the water column during these sampling points. Arrows show the expected slope of -1 (i.e., 1 mol DIC produced per mol DO consumed) for aerobic heterotrophic respiration. Note that the slope of the regression line is much steeper than -1, indicating that aerobic metabolism cannot fully account for water column DIC changes.

At both the creek and mouth sites, DIC concentrations during ebb tide increased steadily (by 0.6–1.9 mmol L^{-1}) before reaching a maximum ~1 h before low tide at the mouth site and slightly after low tide in the creek (Fig. 3). Maximum concentrations at the creek site were always greater than at the mouth site. Similarly, Cai et al. (2000) reported that DIC concentrations in a Georgia salt marsh creek were up to two times greater than in the adjacent river. Because our measured ebb tide concentrations were up to 1.9 mmol L^{-1} greater than predicted by the DIC versus salinity regression equations of Raymond et al. (2000), we suggest that local processes occurring within the marsh–tidal creek system had a strong effect on ebb tide DIC concentrations. Within marsh tidal creeks, DIC can be affected by in situ autotrophic and heterotrophic activity, the mixing of creek water with other end members (e.g., river water, marsh pore water, and groundwater) and CO_2 exchange with the atmosphere. Water column CO_2 concentrations during this study (800 to >20,000 ppm) were 2–69 times greater than atmospheric equilibrium; therefore, the creek was a source of CO_2 to the atmosphere with marsh-atmosphere CO_2 fluxes of 0.3–38 mmol C m^{-2} water h^{-1}. The inputs of DIC from water column and subtidal sediment respiration were estimated using changes in DO over the tidal cycle (Fig. 2) and assuming a respiratory quotient of 1 (i.e., 1 mmol CO_2 produced per 1 mmol O_2 consumed). Although large decreases in DO during ebb tide corresponded with peaks in DIC (compare Figs. 2, 3), respiration in the water column and creek sediments could explain <0.2 mmol L^{-1} of the observed 0.6–1.9 mmol L^{-1} DIC enrichment during ebb tide. The importance of water column respiration will be less if the drainage of anoxic pore water from marsh sediments is sufficient to influence oxygen concentrations in the creek. Across all months and at both the creek and mouth sites, DO and DIC were negatively correlated ($r^2 > 0.57$, $p < 0.001$) with a slope of ~4 mmol DIC produced per mmol DO consumed (Fig. 4). Because this slope is steeper than expected for aerobic heterotrophic respiration (i.e., a respiratory quotient of 1), we suggest that the marsh is ''imprinting'' water in the tidal creek system by either adding DIC and/or removing O_2 (e.g., sul-

fate reduction generates carbonate alkalinity and/or reduced species such as Fe[II] are exported from marsh sediments and are chemically oxidized in the water column). Because DIC in tidal creek waters was always supersaturated with respect to the atmosphere and could not be completely explained by respiration within the creek, there must have been an allochthonous source(s) of high-DIC water that was mixing with the creek and river waters.

Carbonate species distribution—Water draining from the marsh was supersaturated with dissolved CO_2 and therefore emitted CO_2 to the atmosphere by diffusive evasion. Although the equilibration of dissolved CO_2 with the atmosphere will shift the carbonate equilibrium, CO_2 evasion does not affect the carbonate alkalinity, unless carbonate precipitation occurs as a result. Thus, carbonate alkalinity can act as a longer-term sink for carbon and is subject to transport through the estuary to the coastal ocean. To determine whether the marsh-derived DIC represents an atmospheric source (CO_2) or an estuarine sink (carbonate alkalinity) for inorganic carbon, measured pH and DIC concentrations were combined with equations from Park (1969) to calculate the equilibrium partitioning between carbonic acid (H_2CO_3, primarily as hydrated molecular CO_2), bicarbonate (HCO_3^-), and carbonate (CO_3^{2-}). For the pH range observed in the marsh tidal creek (6.4–7.2, Fig. 2), CO_3^{2-} was a minor fraction (<1%) of total DIC. The observed pH decreases during ebb tides (Fig. 2) caused the fraction of CO_2 in the total DIC pool to increase relative to carbonate alkalinity, with the highest proportion of CO_2 (up to 38%) occurring near slack low tide, when DIC concentrations were greatest. The composition of DIC exported from the marsh was similar in June and November (CO_2, 21%–23%; HCO_3^-, 78%–79%). Because of higher salinity in August (Fig. 2), a greater fraction (88%) of DIC was as HCO_3^- during this month. When averaged over ebb tides for all sampling dates, the average composition of DIC exported from Sweet Hall marsh was 19% (±5%) dissolved CO_2 and 81% (±5%) HCO_3^- and CO_3^{2-}. During years with more rainfall and freshwater input, the carbonate equilibrium is likely to shift toward increased dissolved CO_2 because of lower salinities and decreased sulfate reduction rates (an alkalinity source). Changes in this equilibrium will affect the role of the marsh as an atmospheric source or estuarine sink of inorganic carbon.

High CO_2 concentrations in marsh tidal waters (0.03–0.82 mmol L^{-1}) lead to calculated evasion rates of 0.3–38 mmol C m^{-2} water h^{-1} (range includes tidal and seasonal variability and k values from 1.6 to 4.7 cm h^{-1}). These fluxes are comparable to those reported for other CO_2-supersaturated systems, including river estuaries along the east coast of North America (−0.1 to 11.4 mmol C m^{-2} h^{-1}; Raymond et al. 1997, 2000; Cai and Wang 1998) and several western European estuaries (0.4–32 mmol C m^{-2} h^{-1}; Frankignoule et al. 1998; Hellings et al. 2001). In the present study, CO_2 evasion was considerably higher when water was confined to the tidal creeks (0.6–38 mmol C m^{-2} water h^{-1}) versus when the marsh surface was flooded (0.3–8.8 mmol C m^{-2} water h^{-1}). Because the area of tidal creeks at Sweet Hall is small relative to the total marsh area, total (i.e., marsh-derived + riverine-derived) CO_2 efflux was considerably lower when normalized to marsh area (Jun, 7.5–52.2 mmol C m^{-2} marsh d^{-1}; Aug, 9.4–52.1 mmol C m^{-2} marsh d^{-1}; and Nov, 4.9–29.9 mmol C m^{-2} marsh d^{-1}). The efflux of marsh-derived CO_2 accounted for 10%–13% (Aug) to 28%–41% (Jun and Nov) of the total CO_2 evasion and reflected seasonal differences in salinity.

Table 1. Marsh porewater DIC concentrations. Samples were collected within 1 h of low tide along a transect extending from creek bank (0 m) to the marsh interior (30 m; Fig. 1). nd, no data.

Distance (m)	Depth (cm)	DIC (mmol L^{-1})		
		Jun	Aug	Nov
1	5	1.14	2.43	2.10
1	15	3.11	4.86	3.66
1	25	nd	2.15	nd
15	5	2.70	5.56	3.65
15	15	4.66	6.73	5.45
15	25	4.68	6.60	4.58
30	5	3.22	4.69	2.47
30	15	3.99	3.52	3.68
30	25	4.22	2.75	3.09

Pore-water DIC concentrations—With the exception of the shallow creek bank sipper in June and November, all pore-water DIC concentrations (1.14–6.73 mmol L^{-1}) were greater than those measured in the tidal creek or at the creek mouth (Table 1). Therefore, inputs of marsh pore water to the creek via drainage or diffusion may explain the tidal patterns in water column DIC. Pore-water DIC concentrations were generally higher below 5 cm depth; this was likely due to water residence time within marsh sediments. Using a vertical infiltration rate for Sweet Hall marsh of 0.15–2.77 L m^{-2} $tide^{-1}$ (water column to marsh sediments; Reay 1989), an average dry sediment bulk density of 0.408 g cm^{-3} (Neubauer et al. 2002), and an average sediment water content of 67% by mass (S.C.N., unpublished data), it takes 47 to >800 d to completely replace all pore water to a depth of 30 cm. Thus, although shallow (5 cm) pore water can exchange readily with overlying water when the marsh is flooded, deeper pore water turns over slowly; this allows DIC produced by sediment heterotrophic processes to accumulate in deeper sediments. The distribution of flow paths within marsh sediments will determine how much of this high DIC pore water drains into intertidal marsh creeks.

Whole marsh DIC flux—Previous studies that have examined estuarine DIC dynamics have suggested a tidal marsh source of DIC to explain observed DIC concentrations and CO_2 supersaturation within the main stem of the estuary (e.g., Cai and Wang 1998; Cai et al. 1999; Raymond et al. 2000). The consistent increase in DIC during ebb tide (Fig. 3) and the higher DIC_{creek} versus DIC_{river} concentrations support the idea that the marsh was a source of DIC to marsh creek waters. Because the tidal DIC trends were similar at the creek mouth (but somewhat less in magnitude), we suggest that the DIC in water draining from the marsh was exported to the adjacent river.

The DIC export rates calculated using a model of water

Table 2. Ebb tide DIC export and CO_2 evasion from Sweet Hall marsh. Export and evasion rates are for marsh-derived (not total) DIC and CO_2. The DIC export rate includes hydrological export and CO_2 evasion. The DIC export rates and the composition of exported DIC ($\pm$SD; $n = 3$) are provided for model output over the range in $D_{full.}$ Less than 1% of all DIC was exported as CO_3^{2-}. Evasion rates of marsh-derived CO_2 are provided for the range in D_{full} and k values of 1.6, 2.4, and 4.7 cm h^{-1} ($\pm$SD, $n = 9$).

	Ebb tide DIC export (mmol C m^{-2} d^{-1})		DIC composition (%)		Ebb tide CO_2 evasion (mmol C m^{-2} d^{-1})	
Date	Range	Average	HCO_3^-	CO_2	Range	Average
Jun 1999	37–134	82 ± 49	77 ± 1	23 ± 1	1.4–11.8	4.5 ± 3.2
Aug 1999	36–101	66 ± 33	88 ± 0	12 ± 0	0.6–4.0	1.9 ± 1.2
Nov 1999	20–49	33 ± 15	79 ± 3	21 ± 2	0.8–4.8	2.1 ± 1.2

transport through the marsh were similar in June and August (82 ± 50 and 67 ± 33 mmol C m^{-2} d^{-1}) and lower in November (33 ± 15 mmol C m^{-2} d^{-1}; Table 2). These rates are comparable to marsh–water column DIC fluxes of 54–126 mmol m^{-2} d^{-1} for Sapelo Island marsh, Georgia (Cai et al. 1999). We calculate that CO_2 evasion during ebb tide results in the loss of 3%–7% of the exported DIC to the atmosphere (Table 2). There was an exponential relationship between the daily DIC export rate and average daily water temperature, with calculated Q_{10} values ranging from 1.6 to 2.0. These Q_{10} values are similar to the range of 1.9–3.2 reported for other respiratory fluxes (CO_2 respiration and gross nitrogen mineralization) in Virginia tidal marshes (Anderson et al. 1997; Neubauer et al. 2000). Similarly, the releases of DOC and phenolic compounds from peat soils are related to temperature, with Q_{10} values of 1.3–1.7 (Freeman et al. 2001). We suggest that temperature controls the production of DIC within marsh and creek sediments, whereas the actual export is driven by hydrologic factors (e.g., tidal amplitude and duration of flooding). The calculated DIC export versus temperature relationships were combined with daily water temperatures at Sweet Hall marsh (CBNERRVA, unpublished data) over a range of D_{full} values to estimate monthly and annual marsh DIC export rates for 1999 (Fig. 5). When calculated for the entire year, the average rate of marsh DIC export was 16.4 ± 8.2 mol C m^{-2} marsh yr^{-1} (Fig. 5). This rate is similar to the range of DIC fluxes (9.3–20.6 mol C m^{-2} yr^{-1}) calculated for five low-salinity marshes in the Cooper and Edistio Rivers, South Carolina, using 2 years of marsh pore-water DIC data (5–10 and 25–30 cm depths) and an estimate of marsh pore-water

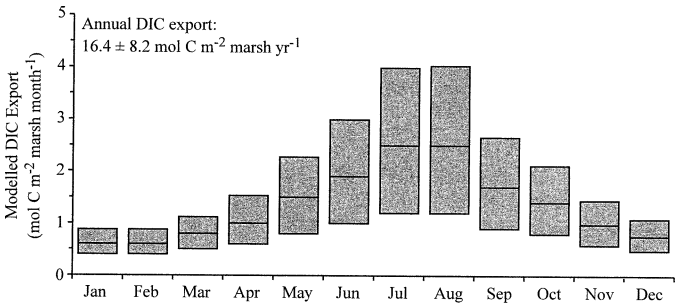

Fig. 5. Modeled monthly and annual rates of marsh DIC export. The solid line near the middle of each bar is the average DIC export for the month; the range in calculated export rates is due to variations in D_{full} values in the export model.

turnover (Neitch 2000). At Sweet Hall, net macrophyte photosynthesis (53.8 ± 7.5 mol C m^{-2} yr^{-1}, Neubauer et al. 2000) and organic carbon inputs associated with sediment deposition (43.1 ± 29.4 mol C m^{-2} yr^{-1}; Neubauer et al. 2002) provide sufficient carbon to account for the calculated DIC export rate. This tidally driven DIC export removes ~30% of the DIC produced annually in marsh sediments (51.6 ± 8.6 mol C m^{-2} yr^{-1}; Neubauer et al. 2000).

DIC export mechanisms—When the surface of a tidal marsh is flooded, the upward diffusion of marsh pore water and the decomposition of plants and detritus on the marsh surface are likely sources of DIC to the water column. When water is confined to the tidal creeks, steep topographic and hydraulic gradients along creek banks can lead to drainage of marsh pore water into tidal creeks. Additionally, DIC fluxes from subtidal sediments into a shallow water column may have a significant effect on creek DIC concentrations. Because the tidal DIC export model is referenced to marsh elevation, we were able to use the model to determine the relative importance of DIC inputs when the marsh was flooded (e.g., via upward diffusion of sediment pore water and the decomposition of plants and detritus) versus inputs occurring when the marsh surface is exposed to air (e.g., pore-water drainage and fluxes from creek-bottom sediments). Using this approach, we estimated that the DIC flux from the flooded marsh represented an average of 32% of the total DIC export for our sampling dates (range, 2%–69% across seasons and D_{full} values). Generally, decreasing the creek-full depth (D_{full}) increased the total DIC export from the system and the relative importance of DIC inputs from the marsh surface, because D_{full} directly controls the predicted depth and duration of marsh flooding. The remaining 68% of the DIC exported from the marsh must have been added to the marsh creeks via pore-water drainage and subtidal respiration when the surface of the marsh was exposed to air. Thus, although the surface area of tidal creeks is only ~5% of the total area of Sweet Hall marsh, inputs of DIC to these creeks may be quantitatively important. Although Cai and Wang (1998) suggested the possibility of significant advective (drainage) DIC losses on the basis of high pore-water DIC concentrations, this route of carbon loss from intertidal marshes has been largely ignored. We suggest that previous estimates that have considered only respiratory and diffusive DIC fluxes during periods of marsh submergence may have substantially underestimated total marsh DIC export.

DIC export and estuarine net heterotrophy—For the York and Pamunkey Rivers (Virginia), Raymond et al. (2000) calculated that net heterotrophy (based on CO_2 evasion and DIC export rates) ranged from 1.7–2.1 $\times$ 10^9 mol C yr^{-1} during their 18-month study. Although we agree with Raymond et al. that this system was net heterotrophic, our data suggest that the observed ''net heterotrophy'' resulted both from in situ respiration of labile organic carbon as well as DIC transported into the river from tidal marshes. Excess DIC is defined herein as that which cannot be explained by conservative mixing between seawater and freshwater or equilibration with the atmosphere. On the basis of incubation experiments, Raymond and Bauer (2000) calculated that bacterial respiration of DOC in the water column could account for 20 $\pm$ 12% of CO_2 evasion in the tidal freshwater Pamunkey River (CO_2 evasion accounted for ~60% of the excess DIC in the system; Raymond et al. 2000) and suggested that the remainder was due to respiration within river bottom sediments, remineralization of POC, or inputs of DIC from tidal marshes. To determine the contribution of tidal marshes to the excess DIC pool in the York and Pamunkey Rivers (i.e., Raymond et al's net heterotrophy), we scaled our estimates of DIC flux from Sweet Hall marsh to the total area of tidal marshes in the estuary. Rates of heterotrophic activity in the sediments and soils of other marshes in the estuary as well as pore-water salinities will determine the amount and speciation (CO_2, HCO_3^-, and CO_3^{2-}) of DIC available for export from each individual marsh. Similarly, the hydrology of each tidal creek and marsh along the river will influence the amount of marsh-derived DIC that is exported to the estuary. Therefore, the actual DIC export from an individual marsh will depend on the specific mechanisms of DIC production, accumulation, and removal in that marsh. Our subsequent calculations and those of Raymond et al. (2000) included the Pamunkey River (which contributes ~70% of the annual flow to the York River) and the York River itself; the Mattaponi River (the other major tributary of the York River) was not included in DIC production or flux estimates.

There must be an input of 1.9 $\times$ 10^9 mol C yr^{-1} to the York River estuary to account for the excess DIC pool in the system (midpoint of range reported in Raymond et al. 2000). As previously mentioned, some of this DIC may be produced by organic matter remineralization in the river itself. Given an annual DIC export rate of 16.4 $\pm$ 8.2 mol C m^{-2} marsh yr^{-1} (Fig. 5) from 5.4 $\times$ 10^7 m^2 of tidal marsh along the York and Pamunkey Rivers (summed from inventories in Silberhorn 1974; Moore 1976; Doumlele 1979; Moore 1980; Priest et al. 1987; Silberhorn and Zacherle 1987), the total export of DIC from tidal marshes could account for 8.9 $\times$ 10^8 ($\pm$4.4 $\times$ 10^8) mol C yr^{-1}, or 47 $\pm$ 23% of the carbon required to support the annual excess DIC production reported by Raymond et al. (2000). Sources of the remaining fraction of carbon to support excess DIC production in the estuary could include water column or sediment metabolism of allochthonous DOC and POC and groundwater inputs to the river. Although we have found no evidence of DOC export from Sweet Hall marsh, an analysis of suspended particulate matter in the creek suggested a possible input of POC from the marsh to the creek (DOC and POC samples were collected at same time as the DIC samples reported herein; see Neubauer 2000). We suggest that our calculation of DIC export may slightly underestimate the actual flux of marsh-derived DIC to the York and Pamunkey Rivers because marsh pore-water DIC concentrations tend to increase toward the saline end of estuaries (e.g., Neitch 2000). However, the total area of salt marshes in York and Pamunkey Rivers is small relative to the area of low salinity tidal marshes in the system, so this effect may be minor. The gradient in marsh pore-water DIC concentrations occurs despite a general increase in total system metabolism (measured as CO_2 efflux from the marsh surface) from saline to freshwater marshes (e.g., Neitch 2000; Neubauer et al. 2000; Miller et al. 2001), primarily because free CO_2 is a greater fraction of the DIC pool in low salinity marshes. The significance of tidal marshes as sources of DIC to estuaries can vary from year to year because of interannual changes in organic carbon inputs in the marsh (e.g., autotrophic production and sediment deposition), microbial metabolic pathways (e.g., salinity-induced changes in the importance of sulfate reduction), and hydrological flushing of the system.

Our annual flux estimates were based on DIC measurements during 3 months (Jun, Aug, and Nov), but rates of estuarine heterotrophy (and excess DIC production) are driven by a suite of interacting biological, chemical, and physical factors and are therefore temporally and spatially variable. In the York River estuary, Raymond et al. (2000) measured the highest rates of excess DIC production in the low salinity regions of the estuary during the summer and autumn (Jun–Oct). Therefore, if tidal marshes are driving the production of excess DIC in the York River, there should be evidence of greater marsh DIC export during the summer versus the winter as well as a larger DIC input to the freshwater reaches of the estuary. Because DIC flux estimates (Fig. 5) and CO_2 gas flux measurements from the marsh surface (Neubauer et al. 2000) reproduce the seasonal patterns of excess DIC in the York River reported by Raymond et al. (2000), there appears to be temporal coupling between processes occurring within tidal marshes and estuarine DIC dynamics. Also, the ratio of marsh to open water is much greater in the Pamunkey River (4.05) than the York River (0.22), which suggests that the relative influence of marshes as DIC sources will be greater in the low salinity reaches of the system. Similarly, Cai et al. (1999) reported that the ratio of intertidal marsh to estuary was a critical factor in constructing CO_2 and O_2 mass balances for the Satilla River, Georgia. The data and modeling results presented herein directly confirm the suggestions that tidal marshes are significant contributors of DIC to estuarine waters and can explain a substantial portion of CO_2 supersaturation and excess DIC production within these systems. Therefore, DIC concentrations in excess of conservative mixing between freshwater and marine end members do not necessarily imply that an estuary is a net heterotrophic ecosystem.

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