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# A marked gradient in $\delta^{13}C$ values of clams *Mercenaria mercenaria* across a marine embayment may reflect variations in ecosystem metabolism

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ABSTRACT: Although stable isotopes of organic carbon ($\delta^{13}C$) are typically used as indicators of terrestrial, intertidal, and offshore organic carbon sources to coastal ecosystems, there is evidence that $\delta^{13}C$ values are also sensitive to *in situ* ecosystem metabolism. To investigate this phenomenon, we examined $\delta^{13}C$ values of filter-feeding hard clams *Mercenaria mercenaria* from 13 locations in Greenwich Bay, a sub-estuary of Narragansett Bay, Rhode Island (USA). The $\delta^{13}C$ values of the clams showed a marked linear gradient of 2‰ over the 4 km length of Greenwich Bay (–19 to –17‰), from lower $\delta^{13}C$ values in the inner bay to higher values at the mouth, where Greenwich Bay joins Narragansett Bay proper ($R^2 = 0.94$, $p < 0.0001$). This is in contrast to previous work that has shown that $\delta^{13}C$ values of clams in Narragansett Bay proper (over 40 km long) are homogenous (mean ± SD, –16.8 ± 0.6 ‰, n = 247). Mean daily pH, temperature, and salinity data from 2 fixed monitoring stations were used to estimate aqueous $CO_2$ ($CO_{2(aq)}$) concentrations in the surrounding water. $CO_{2(aq)}$ concentrations were higher in inner Greenwich Bay than immediately outside of the bay, suggesting that the dissolved inorganic carbon sources supporting phytoplankton production are quite different across the bay. The outer Greenwich Bay clams appear to feed on Narragansett Bay phytoplankton with higher $\delta^{13}C$ values that are grown in a higher pH, more bicarbonate-rich environment. In contrast, the inner Greenwich Bay clams may feed on phytoplankton grown in lower pH water with a greater availability of $CO_{2(aq)}$. The lower $\delta^{13}C$ of $CO_{2(aq)}$ relative to $HCO_3^-$ is reflected in the phytoplankton and in the clams that feed on them. Our work suggests that $\delta^{13}C$ values may be sensitive to changes in inorganic C in estuarine systems, which may confound attempts to use stable isotopes to identify organic carbon sources.

KEY WORDS: Carbon · Stable isotope · Ecosystem metabolism · pH · Greenwich Bay · Narragansett Bay



## INTRODUCTION

Because stable isotopes of carbon ($\delta^{13}C$) fractionate little with trophic level, they have long been used as indicators of terrestrial, intertidal, or marine organic carbon sources for animals and sediments in coastal systems (e.g. Parker 1964, Sackett & Moore 1966, Haines & Montague 1979, Peterson et al. 1985). Ecologists have found $\delta^{13}C$ particularly useful, as values are often quite different among sources. While most upland plants in temperate regions have C3 photosynthetic pathways with characteristic $\delta^{13}C$ values of about –28 ‰ (Peterson & Howarth 1987), marine phytoplankton values typically range from –21 to

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–23‰, and salt marsh grasses with C4 pathways, such as *Spartina alterniflora*, have values from –12 to –14‰ (Haines & Montague 1979, Peterson & Howarth 1987, Cloern et al. 2002). However, recent efforts in food source allocation have demonstrated considerable variation in isotope values among plant species, seasons, and living and dead biomass, suggesting that, in some cases, end-member identification may be more difficult than frequently thought (Cloern et al. 2002, Caut et al. 2009, Dang et al. 2009). In marine systems, the issue is further complicated because different components of the dissolved inorganic carbon (DIC) pool, namely carbon dioxide ($CO_2$) and bicarbonate ($HCO_3^-$), have different $\delta^{13}C$ values, which directly influences $\delta^{13}C$ values of many primary producers (Craig 1953, Raven et al. 2002). All of these factors could contribute to non-conservative mixing of food source $\delta^{13}C$ values among consumers.

As an example of a system that does not fit a traditional end-member mixing model, we found subtidal hard clams *Mercenaria mercenaria* in Narragansett Bay, Rhode Island (USA) with more positive $\delta^{13}C$ values (mean ± SD, –16.8 ± 0.6‰, n = 247) than either terrestrial organic matter or marine phytoplankton (Oczkowski et al. 2008). While intertidal salt marsh plants have more positive $\delta^{13}C$ values than the clams, the area of *Spartina* sp. marsh surrounding the bay is far too small to make a significant contribution to the clam $\delta^{13}C$ values (Nixon et al. 1995). Moreover, the hard clams were isotopically indistinguishable across the bay's 40 km length. These high $\delta^{13}C$ values were consistent with results of an earlier experimental mesocosm study using Narragansett Bay sediment and water, where nutrient-enriched tanks experienced phytoplankton blooms with mean $\delta^{13}C$ values more than 4‰ greater than control tanks (–17.3 ± 2.9 vs. –21.6 ± 1.2‰) (Gearing et al. 1991). The higher values were also reflected in the filter feeders growing in the mesocosms, including *M. mercenaria*, and cannot be explained by source mixing (Gearing et al. 1991). In the cases of both the fertilized mesocosms and the Narragansett Bay hard clams, the more positive $\delta^{13}C$ values were interpreted as reflecting the high productivity of the systems, although the exact mechanisms were unknown (Gearing et al. 1991, Oczkowski et al. 2008).

The extraordinary homogeneity of the Narragansett Bay hard clam $\delta^{13}C$ values contrasts with all other measured biogeochemical parameters in the bay (nutrients, phytoplankton, bacteria, metals, etc.), which show a distinct gradient from the head of the bay to the mouth (Kremer & Nixon 1978, Oviatt et al. 2002). These contrasting results, coupled with equally homogeneous nitrogen isotope values in the Narragansett Bay clams, suggested that phytoplankton formed in the highly productive upper bay are the dominant food source for clams throughout the bay (Oczkowski et al. 2008).

After these results from Narragansett Bay were published, we discovered a surprising exception to this isotope homogeneity in Greenwich Bay, a smaller (12 $km^2$) sub-estuary in the northwest corner of Narragansett Bay. The objective of the present study was to look at how certain physical (circulation) and anthropogenic (eutrophication) factors might dramatically affect carbon sources across small systems only a few km in length, where clams may be feeding on different proportions of *in situ* production and organic matter brought in from adjacent waters. We also explored the evidence for how variations in ecosystem metabolism (the integration of total system production and respiration) may be recorded in hard clams using measurements of $\delta^{13}C$. While numerous studies have documented shifts in $\delta^{13}C$ values associated with changes in DIC (e.g. Parker 1964), which have been reflected in particulate organic matter (Countway et al. 2007), phytoplankton (Fogel et al. 1992), and macroalgae (Finlay 2004), we provide evidence of this variability in higher trophic levels and discuss the implications for traditional food source end-member mixing studies.

## MATERIALS AND METHODS

**Greenwich Bay.** Greenwich Bay (Fig. 1) is a small (12 $km^2$) sub-estuary that branches off the northwest portion of the larger Narragansett Bay (328 $km^2$), with an average depth of 2.6 m (Kremer & Nixon 1978, DiMilla 2006). Direct freshwater inputs from small streams draining into the coves and the effluent from a small wastewater treatment facility together average about 1.3 $m^3\ s^{-1}$ (DiMilla 2006). Salinity in the inner portion of the bay averaged (±SD) 28 ± 1 psu from April through September 2005. During this time period there was no salinity gradient across the bay, as salinity just outside of Greenwich Bay was also 28 ± 1 psu (at North Prudence, Fig. 1; Narragansett Bay Fixed-Site Monitoring Network, DEM 2005). Earlier measurements over an annual cycle showed a mean salinity gradient of only 1.7 psu across the length of Greenwich Bay (Brush 2002). While the mean water residence time (calculated using the freshwater fraction method) is thought to be on the order of about 9 d (DiMilla 2006), it can vary widely from hours to 1 mo (Brush 2002) and circulation in the bay is strongly influenced by winds. Recent numerical modeling efforts (Rogers 2008) have produced results suggesting that under common summer wind conditions a clockwise gyre circulation can develop within Greenwich Bay that may lead to residence times of up to 1 mo. This gyre may prevent or reduce water exchange

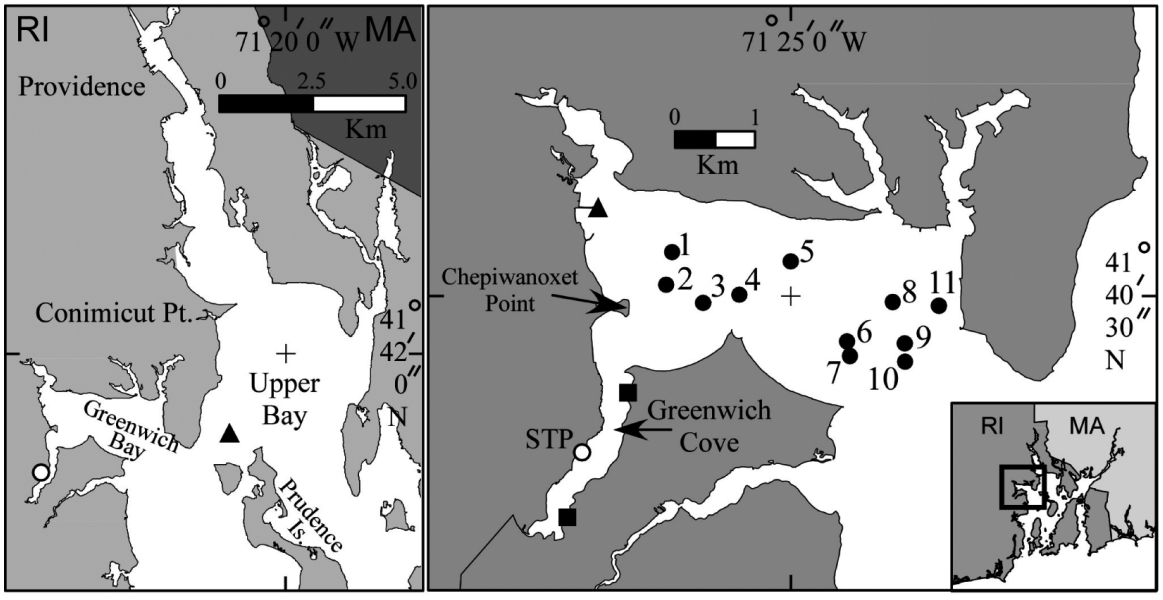


Fig. 1. Upper Narragansett Bay (left panel) and Greenwich Bay (right panel), Rhode Island (USA). Black circles represent locations (Stns 1–11) where clams were collected by the Rhode Island Department of Environmental Monitoring (DEM) and squares show the location of Greenwich Cove clams collected by DiMilla (2006). Black triangles mark the locations of the DEM fixed monitoring sites, in Greenwich Bay and just north of Prudence Island, used to estimate $CO_{2(aq)}$ concentrations. There is a small sewage treatment plant (STP, white circle) in Greenwich Cove that discharged approximately 1 million gallons per day of secondary treated effluent into the cove. Note that the measurements of annual chlorophyll concentrations made by Oviatt et al. (2002) discussed in the text were made in the same approximate location as the DEM monitoring site outside of Greenwich Bay

between the inner and outer portions of Greenwich Bay, thus limiting the influence of Upper Narragansett Bay phytoplankton and increasing the relative importance of local carbon sources to food webs in the inner bay.

Greenwich Bay is one of the most productive areas for hard clams *Mercenaria mercenaria* in Narragansett Bay, with the highest densities occurring at the mouths of the coves (Rice & Goncalo 1995; Fig. 1). This is largely because the coves are permanently closed to harvesting, and the mainstem of Greenwich Bay is frequently closed because of elevated bacterial counts (DEM 2010).

**Hard clams.** Clams *Mercenaria mercenaria* were collected by hydraulic shellfish dredge from 11 sites in Greenwich Bay on 24 June 2005 by the Rhode Island Department of Environmental Management (DEM) as a part of their annual shellfish survey. Water depth at these sites ranged from 2.3 to 5.3 m. Additional subtidal and intertidal clams were collected by DiMilla (2006) on various winter and summer dates in 2004 and 2005 from 2 locations in Greenwich Cove (Fig. 1). The lengths of the clams collected by the DEM ranged from 42 to 98 mm with a mean ± SD of 69 ± 19 mm (n = 60) and the clams from DiMilla (2006) similarly ranged from 28 to 73 mm. Consistent with prior studies conducted in the adjacent Narragansett Bay (Oczkowski et al. 2008), the foot muscle from each clam was carefully removed and dried in a 65°C oven for at least 48 h. The foot muscle tissue was selected to avoid the potentially confounding influences of unassimilated stomach contents and lipid-rich reproductive and metabolically active tissues (Mateo et al. 2008). Samples were then ground into a fine powder using a mortar and pestle and subsamples were weighed in tin capsules for isotopic analysis.

We determined carbon stable isotope values for the clams using a Carlo-Erba NA 1500 Series II Elemental Analyzer interfaced to a Micromass Optima Mass Spectrometer at the US Environmental Protection Agency (EPA) Atlantic Ecology Division in Narragansett, Rhode Island. The carbon isotope composition ($\delta^{13}C$) is expressed as a part per thousand (per mille, ‰) deviation from the reference standard PDB where:

$$\delta^{13}C = [(R_{sample}/R_{standard}) - 1] \times 10^3 \quad (1)$$

and R is the ratio $^{13}C/^{12}C$. Every fifth sample was analyzed in duplicate and differences between samples were < 0.1‰.

**DIC estimates.** Two monitoring stations operated by DEM and the Marine Ecosystems Research Laboratory (MERL) at the Graduate School of Oceanography provided geochemical data from the summer of 2005 and 2008. The first station was located on a marina piling in the northwest corner of Greenwich Bay, and the other on a buoy in upper Narragansett Bay about 4 km from

the mouth of Greenwich Bay (DEM 2005, 2008; Fig. 1). Both stations consisted of 2 sondes, one about 1 m below the surface and the other about 1 m above the bottom. Here we treat only data from the surface sonde, which captured conditions in the water column where phytoplankton production was maximum. The data were collected 4 times per hour, and include temperature, salinity, and pH (National Bureau of Standards scale). We worked with daily averages of these data, available from early June through September 2005 and January to August 2008. We calculated the total alkalinity by treating it as a function of salinity mixing conservatively with river water at 0.4 meq. $l^{-1}$. Our assumption of conservative mixing is based on 17 mo of data from the Taunton River estuary, which supplies one-third of the river water to the bay (Boucher 1991). The results were not qualitatively changed if we used either of the observed extreme values of riverine alkalinity in our area (0 to 1.0 meq. $kg^{-1}$), as salinity differences between the 2 sondes were generally less than 2 psu (URI Watershed Watch, URI 2010b). However, it is important to note that this assumption may not be applicable to all systems, and particularly not to those with large salinity gradients, such as tidal mangrove creeks (e.g. Bouillon et al. 2007). The seawater endmember was taken as 2.32 meq. $l^{-1}$ at a salinity of 35 psu (Millero et al. 1998). Aqueous $CO_2$ ($CO_{2(aq)}$) was estimated as described in Pilson (1998):

$$CA = TA - BA - [OH^-] \quad (2)$$

$$[CO_{2(aq)}] = [CA]\frac{\{H^+\}^2}{K_1^*(\{H^+\} + 2K_2^*)} \quad (3)$$

$$ppCO_2 \times H_{CO_2} = [CO_{2(aq)}] \quad (4)$$

where CA, TA, and BA are carbonate, total, and borate alkalinity, respectively; $\{H^+\}$ is the activity of hydrogen ion; $[OH^-]$ is the concentration of the hydroxide ion; $[CO_{2(aq)}]$ is effectively the concentration of dissolved $CO_2$ gas; $K_1^*$ and $K_2^*$ are constants of the $CO_2$ system calculated for each temperature and salinity; and $H_{CO_2}$ is the Henry's Law constant.

**Statistics.** While station mean $\delta^{13}C$ values were used for statistics on the clam data, the number of individual clams at each station varied widely (from 2 to 10 clams; Table 1). Although more clams per station (i.e. 10) or a consistent sample size would have made the following tests more powerful, we were limited by the number of individual clams available for analysis. A linear regression was performed to determine if the gradient in $\delta^{13}C$ values in clams across the bay was significant. To look for differences between groups of stations, we performed an ANOVA. These statistical tests were performed using JMP V. 7.0.1 statistical software (SAS Institute).

Table 1. *Mercenaria mercenaria*. Mean $\delta^{13}C$ values for Greenwich Bay hard clams. Station locations are shown in Fig. 1. GC: Greenwich Cove

| Station | $\delta^{13}C$ | SD | n |
|---|---|---|---|
| 1 | –18.88 | 0.21 | 10 |
| 2 | –18.91 | 0.17 | 5 |
| 3 | –18.95 | 0.13 | 5 |
| 4 | –18.52 | 0.30 | 4 |
| 5 | –17.97 | 0.10 | 2 |
| 6 | –17.51 | 0.18 | 3 |
| 7 | –17.63 | 0.25 | 3 |
| 8 | –17.58 | 0.03 | 2 |
| 9 | –17.00 | 0.14 | 5 |
| 10 | –17.13 | 0.03 | 4 |
| 11 | –17.03 | 0.10 | 8 |
| Outer GC | –19.59 | 0.26 | 5 |
| Inner GC | –20.14 | 0.38 | 4 |

To see if the time series of pH and $CO_{2(aq)}$ values were significantly different between the 2 monitoring stations in 2005, we took the daily difference between the 2 time series and performed a 1-sided *t*-test to determine that the values were significantly different from zero. Results suggested that the 2 data sets were different for both variables ($p < 0.0001$). We then tested for autocorrelation and performed a Durbin-Watson test to confirm that autocorrelation was occurring. We adjusted the *t*-test p-values for autocorrelation, as described by Pyper & Peterman (1998), by reducing the degrees of freedom, and still found that the differences for both the pH and $CO_{2(aq)}$ data between these 2 stations were significant ($p = 0.0018$ and 0.0043, respectively).

Values are presented as means ± SD unless otherwise indicated.

## RESULTS AND DISCUSSION

### Hard clam $\delta^{13}C$ values

A total of 60 clams were analyzed, with mean $\delta^{13}C$ values ranging from –17.0‰ at the mouth of Greenwich Bay to –20.1‰ in inner Greenwich Cove (Table 1, Fig. 1). When plotted with distance from the western edge, or inner part, of Greenwich Bay, the $\delta^{13}C$ values of the clams show a clear gradient from low to high values from the inner to outer bay (Fig. 2). Clams from the mouth of Greenwich Bay (Stns 9, 10 & 11) had an average $\delta^{13}C$ value of –17.1 ± 0.1‰ (n = 17), similar to values observed in clams from the adjacent Narragansett Bay proper (–16.8 ± 0.6‰, n = 247; Oczkowski et al. 2008). Furthermore, $\delta^{13}C$ values of clams from these stations were significantly greater ($p < 0.0001$) than

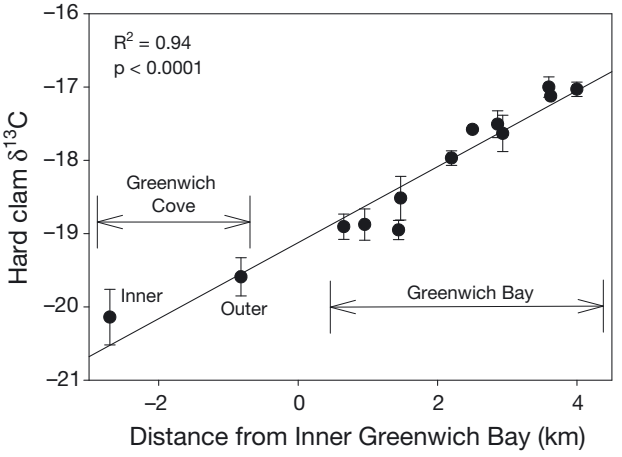


Fig. 2. *Mercenaria mercenaria.* Mean (±SD) $\delta^{13}C$ values of hard clams for each station with distance from inner Greenwich Bay. Greenwich Cove extends from the southwest corner of the mainstem (Fig. 1), and samples were collected in the inner and outer portions of the cove. Removing the Greenwich Cove clam data improves the $R^2$ value to 0.95

those from the 3 westernmost stations (Stns 1, 2 & 3; $\delta^{13}C$ = −18.9 ± 0.2‰, n = 20). Clams from Greenwich Cove fit well into the relationship observed in the mainstem of Greenwich Bay, where clams at the mouth of the cove had mean $\delta^{13}C$ values of −19.6 ± 0.3‰ (n = 5), significantly greater (p = 0.0369) than those from the inner cove (−20.1 ± 0.4‰, n = 4; Figs. 1 & 2).

Clams from throughout Narragansett Bay and the mouth of Greenwich Bay have $\delta^{13}C$ values about 5‰ greater than open ocean marine phytoplankton (−22‰; Fry 2006), suggesting that, despite the high salinity of the system (~28 psu), the filter-feeding clams are consuming a different source of organic carbon than might otherwise be expected. Oczkowski et al. (2008) hypothesized that the higher $\delta^{13}C$ values in Narragansett Bay were the result of locally high pH values (>8) associated with sewage-enhanced phytoplankton productivity in the Providence River Estuary and Upper Bay (Fig. 1). Most marine phytoplankton preferentially use free $CO_2$, but they can also take up bicarbonate ions ($HCO_3^-$; Lucas & Berry 1985, Thompson & Calvert 1994). The ratio of free dissolved $CO_2$ to $HCO_3^-$ decreases rapidly as pH rises (as it does with high rates of photosynthesis), so at high pH, photosynthesizing organisms will take up a greater proportion of carbon as $HCO_3^-$ than at lower pH. Under the conditions in Narragansett and Greenwich Bays in summer, the $\delta^{13}C$ of $HCO_3^-$ is estimated to be about 9‰ more positive than the $\delta^{13}C$ of free dissolved $CO_2$ (calculated using the relationships in Zhang et al. 1995). In consequence, the organic matter formed at higher pH will have higher $\delta^{13}C$ values than that formed at lower pH.

We assumed that the clams from inner Greenwich Bay have lower $\delta^{13}C$ values than the Narragansett Bay clams because their food has lower $\delta^{13}C$ values. This assumption is supported by the work of Gearing et al. (1991) in MERL mesocosm tanks receiving lower Narragansett Bay water, where nutrient-enriched tanks had higher pH and higher phytoplankton and hard clam $\delta^{13}C$ values (−17.3 ± 2.9 and −17.1‰, respectively) than control tanks (−21.6 ± 1.2 and −21.5‰; Oczkowski et al. 2008). We can imagine 2 mechanisms that could lead to a lower $\delta^{13}C$ signature in inner Greenwich Bay: (1) lower $\delta^{13}C$ in the inner estuary clams reflects their use of terrestrial organic matter input (≈−28 ‰) as food, or (2) there is a greater availability of the metabolically favorable $^{12}C$ isotope as $CO_2$ for *in situ* primary production in the inner bay. We reject the first possibility because a preliminary organic carbon budget suggests that the contribution of terrestrial organic matter to Greenwich Bay is small, representing less than 1% of the total organic carbon input to the system. Using an observed relationship between dissolved organic carbon (DOC) and flow from rivers discharging into Narragansett Bay, we estimated DOC loads from rivers to Greenwich Bay to be about 0.5 kg C $d^{-1}$ (Nixon et al. 1995, DiMilla 2006). This estimate also includes ~75% of the groundwater discharging into the system. The remaining 25% enters as direct seepage along the coastline and is highly unlikely to contribute a significant amount of DOC to the system (Urish & Gomez 2004). We used the mean biological oxygen demand value of monthly reported effluent data from 2004 to 2006 from the East Greenwich Sewage Treatment Plant to estimate an organic carbon load from this source of ~19 kg C $d^{-1}$ (US EPA 2010; Fig. 1). While the contribution of particulate organic carbon to Greenwich Bay from intertidal wetlands is unknown, it must be quite small as coastal wetland area comprises less than 1% of the Greenwich Bay watershed and is mainly contained within the coves (wetland data from URI 2010a). For Greenwich Bay as a whole, land-based organic carbon sources are completely dwarfed by *in situ* production by the phytoplankton. Results of $^{14}C$ productivity measurements have suggested that phytoplankton production in Greenwich Bay is almost 7000 kg C $d^{-1}$ (Oviatt et al. 2002). While there is also some production by macroalgae, Granger et al. (2000) estimated this source at between 165 and 493 kg C $d^{-1}$, larger than all the terrestrial inputs but very small compared to phytoplankton. A final potentially significant *in situ* source of organic carbon is production by epibenthic microalgae. While this has never been measured in Greenwich Bay or Narragansett Bay and clearly deserves attention, we interpret the isotopic evidence as suggesting that this is not an important food source for the

hard clams in inner Greenwich Bay. $\delta^{13}C$ values for epibenthic microalgae vary considerably, but they are usually high (~–14 to –17‰; e.g. Currin et al. 1995, Stribling & Cornwell 1997, Wainright et al. 2000, Machás et al. 2003). If epibenthic algae were an important food source, we would expect the trend line in Greenwich Bay to be the opposite from that observed, with clams in the shallower inner bay feeding more on epibenthic algae than those in the deeper outer bay and thus showing more positive $\delta^{13}C$ values.

Our interpretation is that the strong gradient of $\delta^{13}C$ values in Greenwich Bay clams results from the interaction of the predominant circulation patterns in the bay with the high rates of primary production and the resulting high pH and more positive $\delta^{13}C$ of phytoplankton grown in upper Narragansett Bay and the Providence River estuary (Oczkowski et al. 2008). Numerical modeling and studies using Acoustic Doppler Current Profilers have shown that there is a significant flow of upper Narragansett Bay and Providence River estuary water into Greenwich Bay through a deep channel on the northern side of Greenwich Bay, but currents within the inner bay become increasingly weak moving from east to west (e.g. Rogers 2008, Spaulding & Swanson 2008). The very weak tidal circulation may be exacerbated by gyres that develop within the bay under the influence of winds from the southwest that often prevail during summer (Rogers 2008).We hypothesize that inner Greenwich Bay thus operates as a depositional area where significant amounts of organic matter formed in the Providence River estuary and upper Narragansett Bay are deposited throughout the year and respired during the warmer months. The resulting $CO_2$ lowers the pH and thus further increases $CO_2$ by shifting the isotopically more positive $HCO_3^-$ toward more negative $CO_2$. This low $CO_2$ can contribute significantly to *in situ* primary production by the phytoplankton in inner Greenwich Bay, thus setting up a gradient with the clams with the lowest $\delta^{13}C$ values feeding on phytoplankton produced largely within Greenwich Bay and the clams with the highest $\delta^{13}C$ values feeding largely on phytoplankton grown in the higher pH, more $HCO_3^-$-rich waters of outer Greenwich Bay and Narragansett Bay. To explore this hypothesis further, we estimated dissolved $CO_2$ concentrations both inside and immediately outside of Greenwich Bay.

## DIC dynamics

During the summer of 2005, pH was significantly lower and the concentration of $CO_{2(aq)}$ significantly higher in inner Greenwich Bay than in the water outside in Narragansett Bay (Fig. 3). About 85% of the sewage discharging directly into Narragansett Bay is released into the Providence-Seekonk River estuary immediately to the north of the North Prudence sonde station, and approximately 95% of the N entering the Providence River estuary from these point sources is exported to Upper Narragansett Bay (Doering et al. 1990, Nixon et al. 2009; Fig. 1). Sewage nitrogen and phosphorous support a large phytoplankton population that may influence the surrounding water column $CO_{2(aq)}$ concentrations in 2 ways: first, the rate of $CO_{2(aq)}$ uptake during a bloom becomes more rapid than air–sea exchange, thus depleting the $CO_2$; second, the pH of the surrounding water increases, thus increasing the proportion of $HCO_3^-$:$CO_{2(aq)}$ (Chanton & Lewis 1999, Oczkowski et al. 2008). In fact, free $CO_{2(aq)}$ concentrations at the Upper Narragansett Bay station were 33% lower than those of western Greenwich Bay (27 ± 9 vs. 41 ± 16 µmol kg$^{-1}$, respectively). Rapid uptake could also leave the remaining total $CO_2$ enriched in $^{13}C$, the metabolically less favored isotope, as well as force phytoplankton to take up $HCO_3^-$, which has a much more positive $\delta^{13}C$ value (~9 to 10‰ greater than $CO_2$; Zhang et al. 1995, Fry

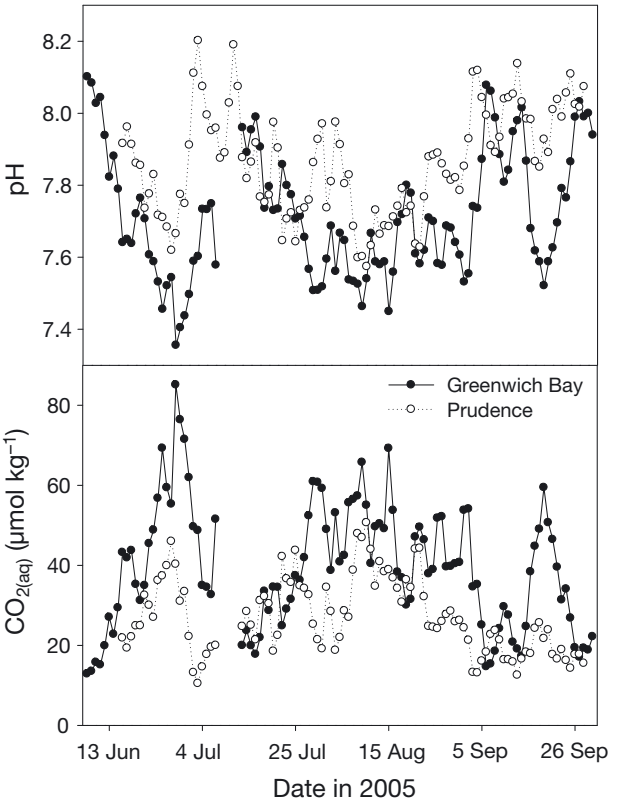


Fig. 3. Mean daily pH and estimated $CO_{2(aq)}$ concentrations from 8 June to 30 September 2005 from one continuously monitoring buoy from the northwestern corner of Greenwich Bay and another from immediately outside of the bay (Prudence Island, see Fig. 1)

2006). Both mechanisms favor more positive $\delta^{13}C$ values in phytoplankton and subsequent filter-feeding clams in Narragansett Bay, with $\delta^{13}C$ values about 5‰ greater than open ocean phytoplankton (Oczkowski et al. 2008).

Higher $CO_{2(aq)}$ concentrations in inner Greenwich Bay indicate that the region is either less productive per unit volume than Upper Narragansett Bay and/or carbon respiration exceeds production in inner Greenwich Bay, at least during summer when the clams are feeding most actively. The amount of time that *Mercenaria mercenaria* spends filtering declines rapidly below 10°C (Loosanoff 1939). The average chlorophyll concentration during the 4 mo of summer measurements in Greenwich Bay was 26.6 mg $m^{-3}$ and at the Narragansett Bay station it was 11.1 mg $m^{-3}$ (DEM 2005), so it does not seem likely that the productivity was less. $^{14}C$ uptake measurements over an annual cycle in 1997–1998 in mid Greenwich Bay and north of Prudence Island showed much higher production per $m^2$ north of Prudence Island, but somewhat higher production per $m^3$ in central Greenwich Bay (Oviatt et al. 2002). Instead, it seems likely that the high $CO_2$ concentration in Greenwich Bay water was due to remineralization of carbon deposited on the sediments during the winter, when productivity greatly exceeded respiration. Recent 2008 data on the partial pressure of $CO_2$ ($ppCO_2$) and pH from Greenwich Bay suggest that net system productivity is greater in the winter than in the summer, as $CO_2$ in the surface water is undersaturated with respect to the atmosphere (about 100 vs. 380 µatm; Fig. 4). As the water becomes warmer, $ppCO_2$ increases 30-fold, the pH drops from 8.5 to 7.5, and the system shifts from net production to net respiration (Fig. 4). This same seasonal pattern is seen in pH measurements collected over annual cycles in the lower West Passage of Narragansett Bay (Hinga 2002). To look more closely at the contributions of respired carbon in inner Greenwich Bay, we can use the pH data from 2008, and typical summer temperature (24°C) and salinity (28 psu), to estimate the total $CO_2$ ($TCO_2$) concentration at 7.5 (approximate summer value, $TCO_2$ = 1948 µmol $kg^{-1}$) and 8.5 (approximate high winter value, $TCO_2$ = 1567 µmol $kg^{-1}$). If we assume that the difference represents net respiration in the summer, which is an underestimate as some of the $CO_2$ is lost to the atmosphere, then about 20% of the $CO_2$ in the water column is from respired organic matter formed in the winter or brought in from Upper Narragansett Bay. If this respired carbon has $\delta^{13}C$ values similar to phytoplankton formed during periods of high productivity (i.e. –17‰), then it follows that $\delta^{13}C$ of the total dissolved $CO_2$ could be reduced by about 3.4‰ relative to the typical values of $\delta^{13}C$ near 0 for total $CO_2$ at summer temperatures, when in equilibrium with the atmosphere (Spiker & Schemel 1979, Zhang et al. 1995, Velinsky & Fogel 1999). Thus, the $CO_2$ available to local phytoplankton would have lower $\delta^{13}C$ values to begin with. While we cannot separate the influence of low respired $\delta^{13}C$ and greater $CO_2$ availability associated with lower pH, both are consistent with lower $\delta^{13}C$ values in phytoplankton produced within Greenwich Bay compared with Narragansett Bay.

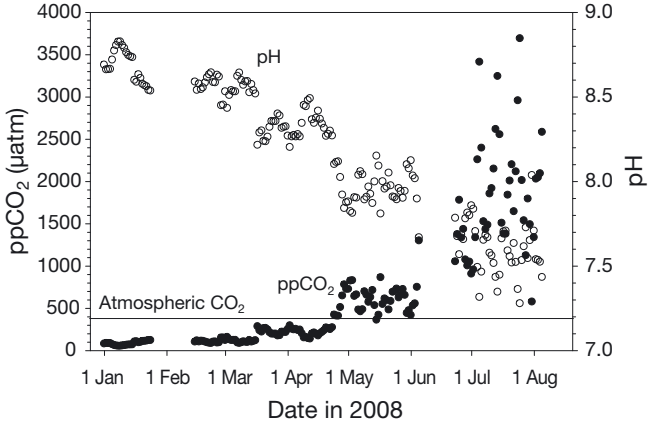


Fig. 4. Greenwich Bay $ppCO_2$ (●) and pH (○) data for 2008. Atmospheric $CO_2$ concentration is denoted by a line at approximately 380 µatm. Thus, the water column is undersaturated with $CO_2$ in the winter and early spring, suggesting net consumption of $CO_2$ by primary producers, and more than 30 times supersaturated with $CO_2$ in the late spring and summer of 2008, suggesting net respiration

This work and that of others (e.g. Gearing et al. 1991, Chanton & Lewis 1999, Oczkowski et al. 2008) demonstrates that $\delta^{13}C$ values in marine consumers reflect more than just conservative mixing of food sources. However, the relative importance of autochthonous primary production, respiration, and the rate of DIC uptake (and its consequences for DIC-C speciation) in influencing $\delta^{13}C$ values in producers and consumers in coastal systems has rarely been discussed in the recent literature. Our data, and the work of others, suggest that the simple 2 end-member mixing models used to assess carbon sources in marine and estuarine systems should be interpreted with caution. In addition, care should be taken to account for all potential carbon sources, including DIC. While there is a substantial body of earlier literature (pre-1980s) discussing $\delta^{13}C$ patterns and trends in estuaries related to DIC dynamics, much of this was published before the importance of $HCO_3^-$ uptake by phytoplankton and macroalgae was fully realized (e.g. Sackett & Moore 1966, Spiker & Schemel 1979). We have readdressed some of these issues, taking the perspective that $HCO_3^-$ can be a significant carbon source to phytoplankton in coastal systems (see Lucas & Berry 1985 for detailed discussion) and that the effects of ambient pH may be reflected in

the $\delta^{13}C$ values of resident consumers. Other factors such as day length and irradiance may also prove to be important (e.g. Thompson & Calvert 1994).

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