

Death by dissolution: Sediment saturation state as a mortality factor for juvenile bivalves

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Abstract

We show that death by dissolution is an important size-dependent mortality factor for juvenile bivalves. Utilizing a new experimental design, we were able to replicate saturation states in sediments after values frequently encountered by *Mercenaria mercenaria* in coastal deposits ($\Omega_{\text{aragonite}} = 0.4$ and 0.6). When 0.2-mm *M. mercenaria* were reared in sediments at $\Omega_{\text{aragonite}} = 0.4$ and 0.6 , significant daily losses of living individuals occurred (14.0% and $14.4\% \text{ d}^{-1}$, respectively), relative to supersaturated-control sediments ($3.9\% \text{ d}^{-1}$). For 0.4-mm *M. mercenaria*, significant mortality occurred under the most undersaturated conditions ($\Omega_{\text{aragonite}} = 0.4$, mortality = $9.6\% \text{ d}^{-1}$), although mortality at $\Omega_{\text{aragonite}} = 0.6$ was not significant (mortality = $2.7\% \text{ d}^{-1}$; control-saturated mortality = $0.2\% \text{ d}^{-1}$). For the largest size-class investigated, 0.6 mm, we show significant mortality for clams under the most undersaturated sediments ($\Omega_{\text{aragonite}} = 0.4$, $2.8\% \text{ d}^{-1}$). To test if buffered sediments would increase survivorship of juvenile bivalves during periods of recruitment, we manually manipulated sediment saturation state by adding crushed *Mya arenaria* shell to a mud flat in West Bath, Maine, U.S.A. Although we increased the average sediment saturation state within retrieved cores from $\Omega = 0.25 \pm 0.01$ to only 0.53 ± 0.06 , numbers of live *M. arenaria* in buffered sediment increased almost three-fold in 2 weeks. Buffering muds against the metabolic acids that cause lowered saturation states may represent a potentially important management strategy to decrease dissolution mortality.

Shallow-water deposits can be significantly undersaturated with respect to both calcite and aragonite and dissolution may occur in surface sediments where juvenile bivalves reside immediately following recruitment (upper few mm, Zwartz and Wanink 1989; Green et al. 1993; Green and Aller 2001). Green et al. (2004b) showed that aragonite-bearing juvenile bivalves (*Mercenaria mercenaria*) dissolve when exposed to sediments undersaturated with respect to calcite and/or aragonite. Dissolution mortality, therefore, is an additional explanation for extreme juvenile mortality ($>98\%$) of shell-bearing, newly settled marine benthic invertebrates in nearshore deposits. Most other studies on juvenile bivalve mortality cite predation, hydrodynamics, temperature, competition, or biological disturbance as the primary factors affecting survivorship (Roegner and Mann 1995; Gosselin and Qian 1997; Hunt and Scheibling 1997). However, the extent to which any of these mortality factors, either alone or compounded, can fully explain the exponential losses of early juvenile bivalves following settlement is unclear (Gosselin and Qian 1997; Hunt and Scheibling 1997). As evidenced by Green et al. (2004b), one largely unexplored and potentially widespread mortality factor that is pertinent to juvenile bivalves is “dissolution mortality” following recruitment to the benthos.

Dissolution as a mortality factor for coastal bivalve populations is important to characterize given current projections of ocean acidification due to anthropogenic effects. Nearshore oceanic waters and estuaries are subject to increasing eutrophication (Vitousek et al. 1997; Cloern 2001) and regional changes in land use (Dove and Sammut

2007), both contributing to increased acidity loading in habitats of commercially important bivalve populations. In addition, model projections for changes to saturation state in the well-buffered open ocean show significant decreases in saturation state in most regions (Gehlen et al. 2007). Less buffered coastal and estuarine habitats are likely to be adversely affected by anthropogenic CO_2 emissions, compounded by previously noted anthropogenic mechanisms lowering potential hydrogen (pH). These coastal habitats and their calcifying organisms are already subject to highly variable pH (Hinga 1992, 2002; Blackford and Gilbert 2007), and additional lowering of pH may result in substantial ecological and economic effects.

We utilized a new experimental design to replicate sediment saturation states in sediment plugs after those values frequently encountered by *Mercenaria mercenaria* in coastal deposits while maintaining overlying water at normal pH values (~ 8.0) and supersaturated conditions. In previous work (Green et al. 2004b), sediment pore water was altered by placing sediment plugs and bivalves into undersaturated seawater. However, coastal marine water is often supersaturated with respect to both calcite and aragonite, meaning these previous experiments were not truly representative of typical in situ conditions. Additionally, we report results from a field experiment measuring recruitment of *M. arenaria* in adjacent CaCO_3 buffered and unbuffered sediment plots. The objectives of this study were to evaluate whether dissolution mortality occurs in *M. mercenaria* when sediments are undersaturated and overlying water saturated with respect to calcium carbonate, and to determine if buffering sediments with ground clam shell from previous harvests could increase recruitment of *M. arenaria*.

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Methods

Laboratory experimental design—We introduced three size classes (0.2, 0.4, 0.6 mm) of the hard shell clam (*Mercenaria mercenaria*) into sediments with manipulated calcium carbonate saturation states of $\Omega_{\text{aragonite}} = 0.4, 0.6,$ and 1.6. Mortality as a function of saturation state and time in each bivalve class was measured separately in three distinct experiments.

Surface sediment for dissolution mortality experiments was collected 48 h prior to the start of each experiment from an intertidal mud flat along the Southern Maine coast (South Portland, Maine, U.S.A.). Experimental sediments were composed of fine-grained, silt- and clay-sized particles and consisted of 3–4% organic carbon and 2–4% CaCO_3 by weight. Surface-sediment (top 1 cm) porosity was typical of fine-grained coastal muds at ≥ 0.9 . The upper 2 mm of the sediment column was collected by scraping with a straight edge and brought back to the laboratory where it was sieved through a 0.25-mm sieve.

Sediment was homogenized by gently stirring and aliquots (~2 cc) placed into each of 45 sediment plugs, and smoothed with a straight edge. Plugs were composed of 12-cm lengths of PVC pipe with a 5-cm outside diameter sealed at the base with a PVC cap. At the top of the pipe a tightly fitting PVC collar was slipped over the outside of the pipe to secure a single 0.22- μm polytetrafluoroethylene (PTFE), hydrophobic membrane filter (175- μm thickness) placed over the PVC pipe opening. The PVC collar was pushed down to produce a sediment depth of 0.75 mm, and resulted in the PTFE membrane beneath the sediment and the PVC collar acted as the walls of the sediment reservoir. The hydrophobic membrane allowed gas to pass across without allowing water to seep through. Air tubing with a 0.6-cm inside diameter (ID) beneath the PTFE membrane connected 15 plugs in series in each of three separate rows of plugs. Tubing from the first plug in the first row (A) was connected to 25% CO_2 balance N_2 tank and an aquarium pump, while the first plug in the second row (B) was connected to 5% CO_2 balance N_2 tank, so that when each tank was turned on, CO_2 flowed through each of 15 consecutive plugs beneath the sediment reservoirs, before exiting from tubing in the last plug of the each row. By altering gas flows through the two separate CO_2 plug rows (A and B), we were able to vary the pH in sediments between rows, giving us two distinct saturation states with respect to aragonite (row A $\Omega_{\text{aragonite}} = 0.4$, row B = 0.6). In the third row of sediment plugs, (row C), an aquarium pump was attached so that only air passed under the sediment layer from plug to plug (controls, $\Omega = 1.6$).

For each specific size-class experiment, the three rows of 15 sediment plugs each were placed into a Plexiglas seawater aquarium (1.83 m \times 0.30 m \times 0.23 m) filled with seawater taken from Casco Bay, Gulf of Maine (salinity ≈ 30). Experiments were run at room temperature ($\sim 20^\circ\text{C}$). At the start of each experiment, *M. mercenaria* were deposited on the surface of each plug (45 total plugs) so that initial densities for each experiment were $\sim 175, 150,$ and 150 plug $^{-1}$ for the 0.2-, 0.4-, and 0.6-mm size classes, respectively. After placement on the plugs, bivalves were

allowed to burrow (generally within several minutes) and equilibrate for a 24-h period before gases were turned on. Over the duration of each experiment, water was changed every 24–72 h and bivalves fed daily a commercially available diatom mixture used for aquaculture (Shellfish Diet 1800; Reed Mariculture).

In the CO_2 -experimental rows A and B, gas flow rates necessary to produce sediment pH of 7.0 and 7.3, respectively, had been predetermined. pH in row C (air flow only) remained stable at 7.9. These pHs, coupled with sediment pore-water alkalinity (Edmond 1970), Cl^- concentrations (YSI 30 Salinity, Conductivity, Temperature Meter) and the experimental temperature (20°C) and salinity (30), were used to calculate carbonate ion (CO_3^{2-}) concentration and pore-water saturation state with respect to aragonite ($\Omega_{\text{aragonite}}$) using the CO_2SYS program. The first and second dissociation constants of carbonic acid in seawater (Mehrbach et al. 1973 refit by Dickson and Millero 1987) were used in the calculations.

To determine whether the addition of CO_2 N_2 gas into two of the three treatments had any potentially confounding effects related to diagenetic redox reactions or associated properties related to organic matter decomposition, we measured dissolved oxygen (O_2) in sediments in multiple plugs in each saturation-state treatment using a microelectrode. If oxygen concentration dropped considerably within the sediment, it would be possible that sulfide or other low redox solutes may contribute to overall mortality. Oxygen penetration into sediment plugs (100- μm intervals) was measured using a Unisense[®] O_2 sensor (50- μm tip diam) and micromanipulator.

Bivalve sampling—Starting with a time-zero sample, triplicate bivalve plugs from each saturation-state treatment were sampled in a time series over the duration of the experiment. The exact time interval of sampling was dependent on bivalve size with the 0.2-, 0.4-, and 0.6-mm bivalves sampled at $\sim 4-, 7-,$ and 10-d intervals, respectively. Mud was removed from the plugs by siphoning through a length of tygon tubing into a sieve of appropriate size for recovering bivalves. Samples were then preserved in 70% EtOH (v/v) buffered with CaCO_3 . Recovered bivalves were stained with Rose Bengal, and live and dead individuals were differentiated and enumerated under a microscope, generally within several days of sampling.

Statistical analyses for dissolution experiments—Simple linear regression analyses were used on the live and dead assemblages within each treatment ($\Omega_{\text{aragonite}} = 0.4, 0.6, 1.6$) and for each size class (0.2, 0.4, 0.6 mm). Assumptions of regression and outliers were checked with standard statistical methods. Data were transformed as needed for violations of assumptions; only the 0.2-mm size-class survival data were log-transformed due to overly influential data points. The effect of saturation state on mortality of each size class was tested by applying *F*-tests to the regression slopes (mortality estimates) and pairwise comparisons were conducted on the three saturation states within each size class with *t*-tests (Sokal and Rohlf 1969). A critical level of $\alpha = 0.05$ was used for all statistical tests.

Specifically, we tested the null hypothesis that, within each size class, the mortality did not change among the three saturation-state treatments.

Field experimental design—A sediment-buffering experiment was run on a clam flat in West Bath, Maine. This clam flat was chosen because historically it had very robust annual *M. arenaria* harvests, but has recently reported diminishing yields. Nonetheless, adult *M. arenaria* are still harvested and, more importantly, analysis of the water column during the spawn of the previous year (2006) showed large numbers of larval *M. arenaria*, suggesting post-settlement mortality as the reason for poor recruitment to the adult population.

During May 2007 we established six study plots (three experimental and three control) in the West Bath clam flat, immediately adjacent to mean-low-water. These plots (8 m × 8 m) ran side-by-side of each other along the long tidal axis of the cove. The corners of each plot were clearly marked using orange survey stakes and remained undisturbed during the entire length of the experiment. During the previous week, discarded *M. arenaria* shell was collected from ~0.5 m of water off a dock from a local shucking facility. The collected shell had been discarded off the dock the previous year and contained no decaying meat. Shell was crushed using a commercial tamper so that the largest particle size was ~0.5 cm. On 15 June 2007 we evenly spread five fish totes of crushed *M. arenaria* shell onto each experimental plot (~75 kg of dried shell or ~1.2 kg m⁻²), resulting in crushed shell material covering ~45% of the sediment surface. Shell material was worked into surface sediments by gentle raking. Although raking altered the physical appearance of the sediment–water interface, all indications of raking disappeared within two tidal cycles. At this point there was no visual difference between the CaCO₃-buffered sediments and the unbuffered controls.

Each day a 20-liter bucket of seawater was collected from the West Bath clam flat, sieved through a 60- μ m sieve and analyzed for the presence of *M. arenaria* larvae. On 09 July 2007 we noticed a sharp decline in numbers of larvae, and assumed this to be representative of the time of transition between the pelagic larval stage and benthic juvenile stage. The next day we began sampling sediments within each sediment plot. One butyrate core (9.5-cm ID) was randomly taken from each of the experimental and control plots during low tide and placed on ice for transport back to the laboratory (~1 h travel time). The surface 1 cm of each core was removed, sieved through a 62- μ m sieve, and all retained material preserved in 70% EtOH, buffered with powdered, lab-grade CaCO₃. Following staining with Rose Bengal, live and dead bivalves were enumerated in the entire sample (sample weights averaged ~110 g wet).

In addition to cores retrieved for bivalve analysis, we randomly removed one core from each plot (six total from the buffered and unbuffered plots) for measurement of saturation state. This was done on the first day of the bivalve sampling. Cores were placed on ice, transported back to the laboratory, and surface-sediment saturation

state (0–1 cm) was measured using pH and alkalinity as described previously.

Statistical analysis for field-buffering experiment—We used a repeated-measures ANOVA to test the null hypothesis that there was no difference in recruitment of *M. arenaria* to control–unbuffered vs. experimental–buffered plots. *M. arenaria* per gram of sediment data were used, because these provided the best-fitting model following Akaike's Information Criteria. In addition, a compound symmetry covariance structure was used, as was the Kenwood–Rodgers method for degrees of freedom (Littell et al. 2006). Assumptions of normality and homoscedascity were checked and met.

Sediment saturation state and pore-water Ca²⁺ in Casco Bay, Gulf of Maine—A GOMEX-2525 box corer (625 cm²) was used to collect bottom sediment and overlying water during June, July, and August (concurrent with the field-buffering experiment) at two stations in Casco Bay, Gulf of Maine. A highly detailed description of these stations is provided in Green et al. (2004a). The GOMEX box corer yielded well-defined, undisturbed sediments, as was evident by the clear water above the sediment–water interface (SWI). Butyrate sub-cores (9.5-cm ID) were removed from the corer and transported on ice back to the laboratory for analysis. In general, water depths were ~7 m, sediments were muddy, consisting of 3–5% organic carbon (~10% loss on ignition), and 1–3% CaCO₃ and had average surface-sediment porosity of ~0.9. Back in the lab, cores were sectioned under N₂ in a glove bag and discrete intervals centrifuged at 5000 revolutions per minute for 5 min. Pore water was filtered through a 0.45- μ m Acrodisc® filter. One aliquot (2 mL) was used to measure total alkalinity (Edmond 1970) and another (10 μ l) was used to measure Cl⁻ using a Labconco Digital Chloridometer. The remaining pore-water sample was acidified (10 μ l 12N HCl mL⁻¹ pore water) and Ca²⁺ analyzed with a precision of \pm 2% on a Perkin Elmer AAnalyst 300 Atomic Absorption Spectrophotometer using an air–acetylene flame. Pore-water saturation states were estimated as described previously.

Scanning electron microscopy of juveniles in dissolution experiments—Using a JEOL JSM-6100 scanning electron microscopy (SEM) with a standard tungsten gun, we evaluated the condition of *M. mercenaria* shells as a function of time during the laboratory experiments. Larval bivalve samples recovered from the experiment were first treated with a 1% hydrogen peroxide solution to remove excess organics, rinsed in purified water (reverse osmosis), treated in a 100% EtOH solution for 3 min, and then mounted onto presputtercoated (Au Pd film) glass cover-slips treated with 1% Poly-L-lysine for adhesion. Mounted samples were then carbon-coated (Denton Vacuum DV1 Carbon Coater) and cover-slips mounted on stubs using 2-sided carbon tape. Samples were viewed at 5–10 kV (accelerating voltage) from a distance of 15–20 mm to improve resolution.

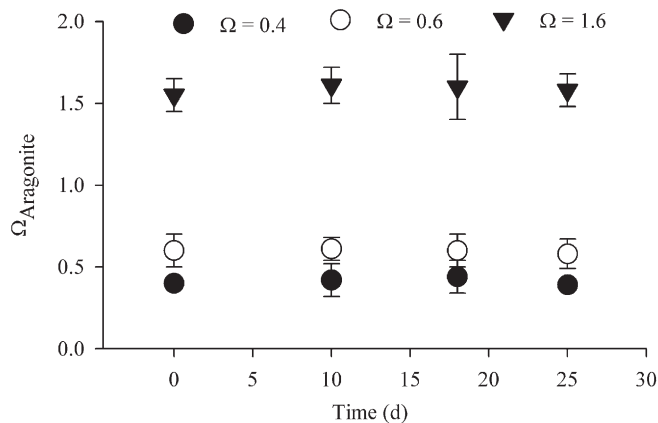


Fig. 1. Average values for aragonite saturation states from sediment plugs.

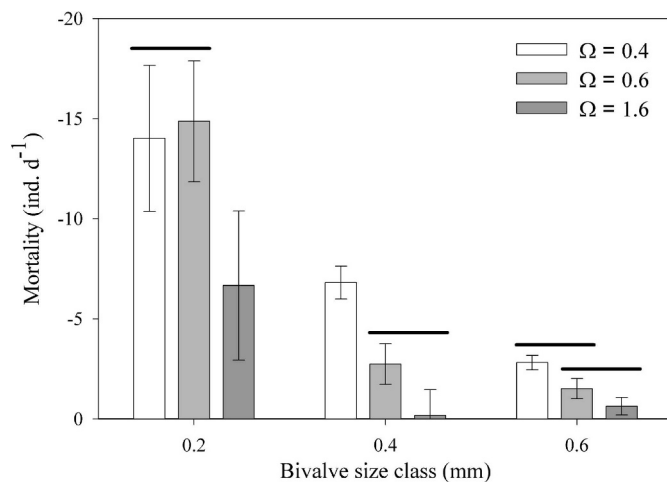


Fig. 2. Mortality estimates from the regression analyses for each bivalve size class, and experimental saturation state. Error bars are the standard error of the calculated slopes. Shared line above the bars indicates no significant difference between mortality at given saturation states.

Results

Laboratory dissolution mortality experiments—Thermodynamic analysis: The three different treatments of pore-water saturation state in sediment plug rows A, B, and C remained constant over the duration of each experiment at $\Omega_{\text{aragonite}} = 0.4, 0.6, 1.6$. The overlying water saturation state remained nearly identical to that of the supersaturated plugs at $\Omega_{\text{aragonite}} = 1.8$. Data are presented in Fig. 1 for the experimental run using the 0.6-mm size class and are representative of saturation-state data for all three size-class experiments.

Bivalve mortality due to dissolution—Significant mortality of all three size classes occurred at the lowest saturation state (Fig. 2). Plots of live bivalves as a function of time for each size class in the three specific pore-water saturation states are shown in Fig. 3A–C. Simple linear regression was used to determine mortality of juvenile bivalves in each

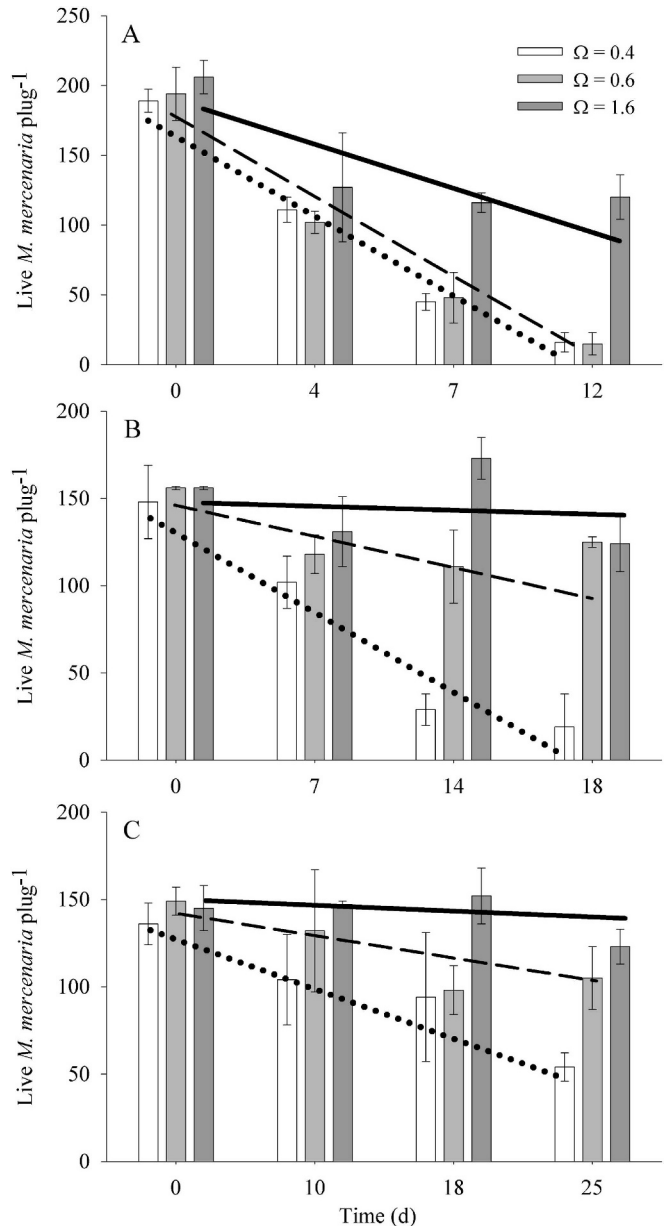


Fig. 3. Mean densities (\pm SD) of live *M. mercenaria* as a function of time in each for each of the three size classes (A = 0.2 mm, B = 0.4 mm, C = 0.6 mm). Lines show regression trend of loss of bivalves over time, where the dotted line is $\Omega_{\text{aragonite}} = 0.4$, the dashed line is $\Omega_{\text{aragonite}} = 0.6$, and the solid line is the $\Omega_{\text{aragonite}} = 1.6$ treatment.

saturation state for each of the three size-class experiments and data are presented in Table 1 as loss of individuals per day. Mortality as percent per day was calculated as the proportion of live bivalves relative to the previous time period, providing instantaneous mortality measurements at each sampling period that were averaged for each size-treatment combination. Statistical effects of saturation state and treatment differences are presented in Table 2.

For the 0.2-mm *M. mercenaria*, significant mortality occurred for clams reared in both undersaturated treatments; $\Omega_{\text{aragonite}} = 0.4$ and 0.6 (Fig. 3A; Table 1), with no

Table 1. Linear regression analyses of surviving *M. Mercenaria* from each size class (0.2, 0.4, 0.6 mm) reared in sediments with three distinct saturation-state ($\Omega_{\text{aragonite}} = 0.4, 0.6, 1.6$). The fit statistics and probabilities for the 0.2-mm size class are natural-log-transformed data. Mortality estimates for the 0.2-mm size class are not transformed. Mortality estimates in % d^{-1} are averages of instantaneous mortality rate at each sampling time.

Size class	Ω	Bivalves d^{-1}	% d^{-1}	Adj. R^2	F -value	ndf	ddf	p -value
0.2	0.4	-14.02	14.04	0.99	53,387.60	1	3	0.0001
0.2	0.6	-14.86	14.42	0.98	239.54	1	3	0.0041
0.2	1.6	-6.66	3.91	0.43	3.32	1	3	0.2098
0.4	0.4	-6.81	9.62	0.94	68.54	1	4	0.0037
0.4	0.6	-2.74	2.73	0.61	7.18	1	4	0.0751
0.4	1.6	-0.17	0.00	0.00	0.02	1	4	0.9023
0.6	0.4	-2.81	2.51	0.94	61.72	1	4	0.0043
0.6	0.6	-1.51	0.77	0.66	8.79	1	4	0.0593
0.6	1.6	-0.64	0.27	0.22	2.10	1	4	0.2431

significant mortality in the supersaturated treatment; $\Omega_{\text{aragonite}} = 1.6$ (Table 1, $p = 0.2098$). Saturation state significantly increased mortality across the 0.2-mm size class ($F_{2,6} = 64.25$, $p = 0.0001$), and both undersaturated treatments had significantly higher mortality than the supersaturated treatment, but not significantly different from each other (Table 2).

For the 0.4-mm *M. mercenaria*, significant mortality occurred under only the most undersaturated conditions (Fig. 3B; Table 1; $\Omega_{\text{aragonite}} = 0.4$). For the $\Omega_{\text{aragonite}} = 0.6$ and 1.6 treatments no significant mortality occurred over the duration of the experiment. A significant effect of saturation state on mortality of the 0.4-mm clams was found ($F_{2,9} = 10.84$, $p = 0.005$), and clams in the $\Omega_{\text{aragonite}} = 0.4$ treatment had significantly higher mortality than in the other two treatments (Table 2).

For the 0.6-mm size class, significant mortality occurred for clams only under the most undersaturated sediments (Fig. 3C; Table 1; $\Omega_{\text{aragonite}} = 0.4$). Significant treatment effects of saturation state on mortality were found in the 0.6-mm size class ($F_{2,9} = 9.69$, $p = 0.006$), and only mortality in the $\Omega_{\text{aragonite}} = 0.4$ and 1.6 treatments were significantly different from each other (Table 2).

Carbonate-buffering field experiment—Sediment buffering with crushed shell (CaCO_3) increased the alkalinity, pH, and aragonite-saturation state relative to the unbuffered control plot in West Bath, Maine (Table 3). Applying crushed *M. arenaria* shell on the experimental plot resulted in an alkalinity, pH, and $\Omega_{\text{aragonite}}$ of 2.8, 7.31, and 0.53, respectively. This compares to 2.45, 7.04, and 0.25 for alkalinity, pH, and aragonite in cores recovered from the unbuffered control plot. So, although sediment saturation state was still undersaturated in buffered sediments, addition of shell in the quantities used here increased saturation state by a factor of two.

As shown in Fig. 4, over the duration of the experiment, a steady increase in *M. arenaria* recruiting to the sediment with carbonate buffer occurred relative to the control plots. As shown in Table 4, CaCO_3 buffering produced a highly significant difference in recruitment between the buffered and control treatments ($p = 0.0059$). The time effect was significant as well ($p = 0.025$) and indicates changes in overall recruitment over time. A significant treatment \times time interaction ($p = 0.0166$) highlights the clear differences in recruitment into the buffered and control plots over the course of the experiment (Fig. 4).

Table 2. Statistical effects of saturation state on bivalve mortality for each bivalve size class. The F -values show statistically significant effects of saturation state on all bivalve size classes, while t -tests show differential effects of each saturation state with size class.

Size class	Differences	ndf,ddf	F -value	t -value	p
0.2-mm bivalves saturation state	—	2,6	64.25	—	0.0001
	0.4 vs. 0.6	1,4	—	0.87	0.4325
	0.4 vs. 1.6	1,4	—	7.00	0.0022
	0.6 vs. 1.6	1,4	—	6.45	0.0030
0.4-mm bivalves saturation state	—	2,9	10.84	—	0.0046
	0.4 vs. 0.6	1,6	—	3.10	0.0211
	0.4 vs. 1.6	1,6	—	4.33	0.0049
	0.6 vs. 1.6	1,6	—	1.56	0.1721
0.6-mm bivalves saturation state	—	2,9	9.69	—	0.0057
	0.4 vs. 0.6	1,6	—	2.09	0.0811
	0.4 vs. 1.6	1,6	—	3.85	0.0085
	0.6 vs. 1.6	1,6	—	1.30	0.2407

Table 3. Geochemical data from control and experimental (buffered) core removed from each plot in the experimental area of West Bath, Maine, U.S.A. Alkalinity units are meq L⁻¹.

Control alkalinity	Buffered alkalinity	Control pH	Buffered pH	Control $\Omega_{\text{aragonite}}$	Buffered $\Omega_{\text{aragonite}}$
2.56	2.75	7.03	7.33	0.26	0.50
2.44	2.84	7.04	7.34	0.25	0.60
2.35	2.80	7.05	7.30	0.25	0.50

Sediment-saturation state and pore-water Ca²⁺—Despite supersaturated overlying water ($\Omega_{\text{aragonite}} \sim 3.5\text{--}4$), pore water in sediments at both stations sampled in Casco Bay, Maine was undersaturated with respect to aragonite (Fig. 5). Highest levels of undersaturation were adjacent to the SWI and pore water tended towards, or exceeded, equilibrium values with depth (5–10 cm). Evidence that dissolution was occurring in these same sediments comes from elevated pore-water Ca²⁺ relative to overlying water concentrations (Fig. 6).

Scanning electron microscopy of dissolving shells—Scanning electron micrographs of representative 0.2-mm *M. mercenaria* reared in sediments maintained at $\Omega_{\text{aragonite}} = 0.6$ are shown in Fig. 7. All bivalve size classes used in these experiments and reared in sediments where $\Omega_{\text{aragonite}} < 1$ showed significant signs of shell dissolution. As a general observation and as depicted in Fig. 7, extensive pitting of ostracum in the umbonal region was recorded after 4 d in all bivalves photographed. Dissolution over the entire region of the ostracum followed (as noted by day 7; Fig. 7B and C), so that extensive regions of the underlying hypostracum became visible and began to dissolve. Lastly, the growing edge, the ventral margin, was observed as being completely corroded within 7 d (Fig. 7C).

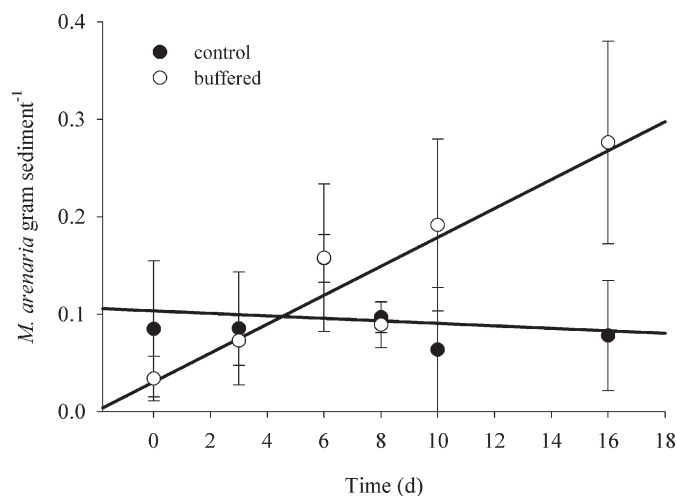


Fig. 4. West Bath field data showing changes in *M. arenaria* as a function of time in sediment cores recovered from buffered and unbuffered muds. Counts are in live *M. arenaria* g⁻¹ sediment in control (unbuffered) and experimental (buffered) sediments.

Discussion

Carbonate saturation in coastal deposits and bivalve calcification—A quantitatively significant proportion of biogenic CaCO₃ produced shoreward of the shelf-break dissolves in both terrigenous and carbonate sediments underlying waters saturated with respect to carbonate minerals (McNichol et al. 1988; Rude and Aller 1991; Green and Aller 1999; Green and Aller 2001). Although the importance of this process is generally accepted, skepticism still exists as to the potential effects of sediment saturation state on shell-bearing organisms. That is, can sediment carbonate geochemistry affect population dynamics by dissolution of carbonate-skeleton-bearing benthos?

Coastal deposits that are undersaturated with respect to calcium carbonate may actually represent *normal* geochemical conditions for surface deposits. The saturation state with respect to calcium carbonate is the ion activity product of Ca²⁺ and CO₃²⁻ divided by the solubility product (K_{sp}). If salinity, temperature, and pressure remain the same, primarily changes to CO₃²⁻ concentration will alter saturation state. Unlike the relatively straightforward thermodynamic controls on CO₃²⁻ concentrations in the deep sea (aerobic CO₂ production and CO₃²⁻ titration), the processes responsible for lowering CO₃²⁻ in coastal regions are more environmentally specific. The interplay of seasonal temperature change, spatial heterogeneity, aerobic respiration at the SWI, proton production (lowering pH) during oxidation of reduced metabolites (e.g., NH₄⁺, Mn²⁺, Fe²⁺, acid-volatile sulfur), and additional transport-related controls such as particle reworking and bio-irrigation (Aller 1982; Green et al. 2004a; Jansen and Aherns 2004) all contribute variability in CO₃²⁻. Undersaturated surface sediments have been documented in many coastal regions along the east coast of the United States (Aller 1982; McNichol et al. 1988; Rude and Aller 1991), and are presumably encountered throughout the world in regions with similar sediment types.

During the field-buffering study, for example, we documented $\Omega_{\text{aragonite}}$ in the surface sediments ranging from 0.2 to 0.6 during the months of June, July, and August (Fig. 5) in two coastal stations of Casco Bay, Gulf of Maine (Sta. 1 and 2 from Green et al. 2004a). In

Table 4. Statistical results from West Bath field experiment.

Effect	ndf	ddf	F-value	p
Treatment	1	2.99	49.88	0.0059
Time	5	20.1	3.28	0.0250
Treatment × time	5	20.1	3.64	0.0166

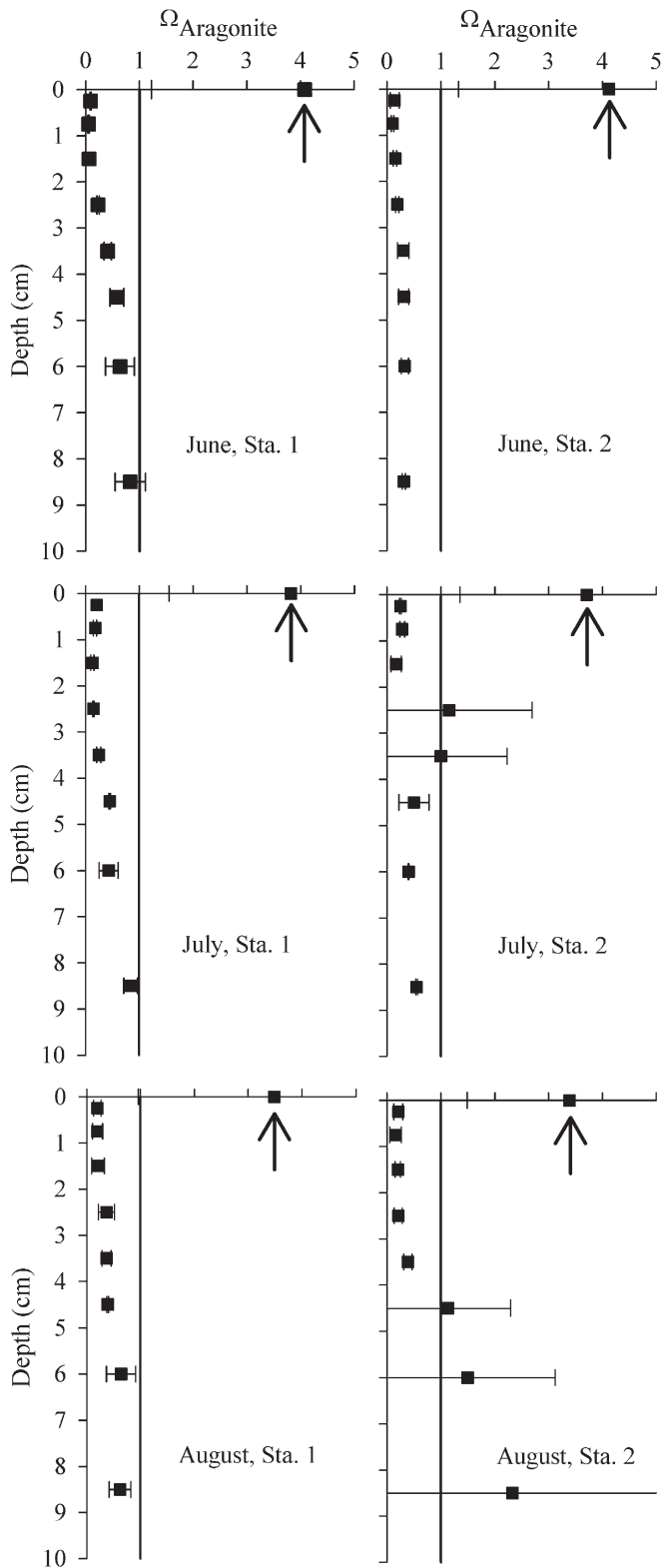


Fig. 5. Aragonite saturation state data for Sta. 1 and 2 in Casco Bay, Gulf of Maine during June, July, and August 2007. Overlying water saturation state plotted at depth = 0, highlighted by arrow. For complete station descriptions see Green et al. (2004b).

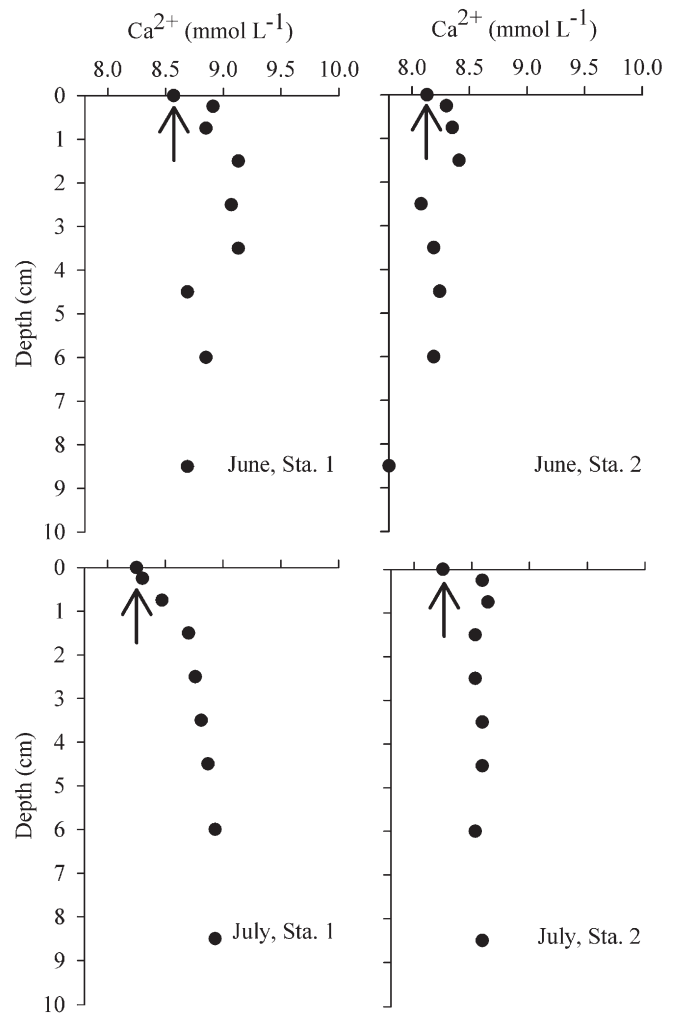


Fig. 6. Pore-water Ca^{2+} for Sta. 1 and 2 in Casco Bay, Gulf of Maine during June and July 2007. Overlying water concentration shown by arrow.

addition, elevated pore-water Ca^{2+} in these sediments (only measured in Jun and Jul) provides evidence that dissolution was occurring (Fig. 6). Coincidentally, the major spawning period of *M. mercenaria* and *M. arenaria* in Southern Maine is June–July. Our laboratory and field results indicate that the measured levels of carbonate undersaturation in the field will result in significant mortality and, therefore, is likely an important factor in the survivorship and abundance of newly settled bivalves.

In this study, we show that death by dissolution appears to be an important size-dependent mortality factor for juvenile bivalves. When sediments are moderately undersaturated with respect to aragonite, even when overlying water is supersaturated, significant dissolution mortality of the assemblage occurs. At $\Omega_{\text{aragonite}} = 0.4$, all size classes studied show significant mortality relative to control-saturated sediments ($\Omega_{\text{aragonite}} = 1.6$) with dissolution losses equivalent to 14.0%, 6.8%, and 2.8% d^{-1} for the 0.2-, 0.4-, and 0.6-mm bivalves, respectively (Table 1). Even at the higher $\Omega_{\text{aragonite}}$ value of 0.6, nearly identical dissolution losses were seen for the 0.2-mm size class

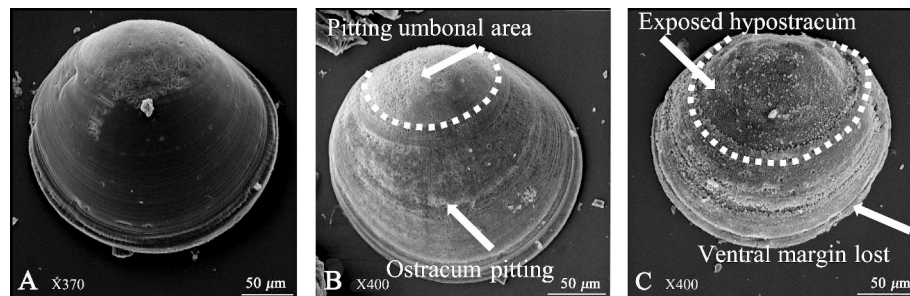


Fig. 7. Scanning electron micrographs (SEM) of representative 0.2-mm *M. mercenaria* reared in sediments maintained at $\Omega_{\text{aragonite}} = 0.6$. Clams were removed from sediment plugs at 0, 4, and 7 d (A, B, and C, respectively). Magnification and scale bars are shown, as well as significant effects to various parts of the shell.

(14.4% d^{-1}). The actual threshold saturation state for significant dissolution mortality of juvenile *M. mercenaria* following recruitment to coastal muds is, therefore, a function of size; as size increases bivalves are less susceptible to death by dissolution. For example, the 0.2-mm individuals had significant mortality at $\Omega_{\text{aragonite}} = 0.6$, while the larger individuals (0.4 mm and 0.6 mm) had significant mortality only at $\Omega_{\text{aragonite}} = 0.4$. The actual threshold saturation state where significant dissolution mortality occurs, presumably lies somewhere between $\Omega_{\text{aragonite}} = 0.6\text{--}1.0$ for 0.2-mm *M. mercenaria* and $\Omega_{\text{aragonite}} = 0.4\text{--}0.6$ for 0.4-mm and 0.6-mm *M. mercenaria*.

The extent of dissolution mortality will be controlled by differences in the rates of external shell dissolution and internal shell biocalcification. Shell formation in bivalves is an internal process where the mantle secretes organic material into the extrapallial fluid between the mantle and shell or directly onto the inner shell surface. Ca^{2+} , HCO_3^- , and CO_2 passes through the epithelium to the extrapallial fluid where crystals of calcium carbonate are formed under saturated or supersaturated conditions. In bivalves, concentrations of Ca^{2+} , HCO_3^- , and CO_2 are physiologically controlled and fluctuate independently of concentrations in the surrounding seawater. Actual deposition occurs from the extrapallial fluid onto either the organic matrix or onto previously precipitated crystals. Presumably, external shell dissolution is occurring even during active internal shell precipitation in growing juveniles.

We provide visual evidence of external shell dissolution using SEM (Fig. 7). Obvious dissolution resulted in radical changes in the surface relief of bivalve shells after very short periods. Likewise, the jagged surface of individual crystal-lites suggests that dissolution rates were controlled by surface reaction and not transport processes (Morse 1983). Representative live juveniles from the 0.2-mm size class were removed from the $t = 0$ -, 4-, and 7-d samples from the $\Omega_{\text{aragonite}} = 0.6$ treatment and photographed. Within 4 d (Fig. 7B) juveniles show substantial shell pitting of the ostracum, with greatest amounts occurring on the older, umbonal region. By day 7 (Fig. 7C), the entire ostracum is gone over large portions of the bivalve and the internal carbonate shell layer, the hypostracum, is clearly visible. In addition, the newest precipitated shell along the ventral margin is largely gone. Although not provided, SEM taken

from bivalves recovered after shorter durations of exposure to undersaturated muds and/or at lower saturation states also showed significant shell decay. In general, smaller bivalves showed greater degree of shell loss more quickly than larger individuals and, within any given size class, shell loss was far more extensive at lower $\Omega_{\text{aragonite}}$ values. Combating these rates of external shell dissolution for many more days would prove difficult. Experimental results coupled with SEM suggest that external shell dissolution occurs when bivalves are exposed to undersaturated sediments and that longer exposure translates to greater regions of dissolution and potentially increased mortality.

Death by dissolution and other post-settlement factors—It is widely accepted that local bivalve abundance is controlled by factors related to early life history, survival, and habitat selection (Gosselin and Qian 1997, Hunt and Scheibling 1997). The extreme post-settlement loss of juvenile bivalves from marine sediments has most often been attributed to predation (Ólafsson et al. 1994), competition (Ahn et al. 1993), and hydrodynamic dispersion (Roegner et al. 1995). Hydrodynamic dispersion may move individuals on the order of 10s to 100s of meters, but does not necessarily result in a net population loss (Emerson and Grant 1991). It is most likely that a suite of factors acting on different size classes will determine the success of newly settled cohorts, though one factor not adequately addressed is dissolution mortality. Limited evidence suggests that predation on juvenile bivalves is a size-selective process with predators actively selecting for larger individuals (>1 mm; Hunt and Scheibling 1997; Richards et al. 1999; Hunt and Mullineaux 2002). It is possible that meiofaunal species may be important predators on newly metamorphosed bivalves (Newell et al. 2000), though additional studies are needed in this area. Our current results and previous studies (Green et al. 1998; Green et al. 2004b) indicate that *M. mercenaria* $<1\text{--}2$ mm are most susceptible to dissolution mortality, and that $1\text{--}2$ mm may constitute an escape size for dissolution mortality in this species. Dissolution mortality resulted in $>90\%$ mortality in the smallest size class (0.2-mm; Fig. 3A) and well over 50% mortality in other size classes (Fig. 3B, C). These high mortality rates measured in the absence of

predation will likely be compounded by increased susceptibility to predation in situ when shells have been compromised by dissolution. Furthermore, the results for the field-buffering experiments indicate that buffered sediments increase recruitment of *M. arenaria*, though it is possible that buffered sediments either decreased mortality or increased settlement due to chemical cues (Engstrom and Marinelli 2005), or some combination of the two. Overall our study highlights the potential importance of sediment saturation state as a post-settlement mortality factor to newly set juvenile *M. mercenaria* and *M. arenaria*.

What remains unclear is the following: what, ultimately, is killing juvenile bivalves when their shells dissolve? Without the protection of an intact carbonate shell, juveniles are exposed to whatever the biotic and/or abiotic conditions that exist in situ, and for which the shell was deemed evolutionarily necessary to begin with. We observed bivalves daily during each experimental run using a specially designed dissecting microscope mounted on top of the seawater chamber. We noted that even in the most undersaturated treatments dissolving bivalves were seen siphoning for food in a manner similar to juveniles in the control-saturated treatment. These feeding activities were common in all experimental trials, despite severe shell dissolution of the animal. At some point the shell integrity is so far compromised that death occurs to the bivalve by some factor (i.e., bacterial infection, osmo-regulation issues, temperature change, etc.). The ultimate death of juveniles is what we document here. Without shell dissolution first occurring, mortality rate is significantly reduced, as evidenced by the control-saturated survivorship data (Fig. 3; Table 1).

We measured dissolved oxygen in sediments in each treatment using micro-O₂ sensors and noted that, even in the lowest pH treatments, O₂ at the base of the sediment layer was nearly 50% saturated. This compared to ~75% saturation of the control-saturated treatment. The difference in sedimentary O₂ resulted from addition of CO₂ N₂ gas to the chambers below the undersaturated treatments A and B. However, the presence of O₂ in all treatments means that bacterial respiration and C-organic degradation was being accomplished aerobically and no other sequential oxidant was being used. Hence, mortality differences between treatments cannot be explained by differential metabolite production and build-up, for example sulfide.

Acidification effects and management strategies—Acidification due to atmospheric release and subsequent aquatic absorption of anthropogenic CO₂ is only one of several factors likely to lower pH in coastal aquatic ecosystems. Open-ocean chemistry and carbonate mineral saturation state has been altered as a result of CO₂ hydrolysis in seawater and the associated CO₃²⁻ titration (Gehlen et al. 2007). However, estuaries (especially river-dominated) are often highly heterotrophic and may have CO₂ concentrations greater than atmospheric concentrations (Cai and Wang 1998; Frankignoulle et al. 1998; Gattuso et al. 1998). Increased atmospheric CO₂ has the potential to slow CO₂ evasion from these heterotrophic systems. Additionally,

several other anthropogenic effects have the potential to increase acidity of coastal ecosystems. Nutrient and allochthonous organic-matter loading to estuarine and coastal ecosystems (i.e., eutrophication and runoff) and subsequent respiration of this organic matter will increase acidity (Soetart et al. 2007). Additionally, coastal waters are disproportionately susceptible to acid rain effects on pH (Doney et al. 2007). With the highly variable pH found in many coastal systems (Hinga 2002; Blackford and Gilbert 2007), further acidity loads may increase the already extreme mortality found in many calcifying benthic invertebrates. Changes in coastal ocean chemistry as a result of anthropogenic CO₂ injection, coastal eutrophication, and acid rain may alter existing biological communities of benthic shell-forming organisms. Predicting the combined acidification effects on coastal biogeochemistry poses a formidable challenge. However, buffering sediments with CaCO₃ is one strategy that may help preserve commercially and ecologically important sediment dwelling bivalves in coastal areas.

If death by dissolution is a common phenomenon for shell-forming infauna in coastal muds, it might be possible to substantially increase clam abundance by mitigating dissolution through buffering sediments. With settlement densities of 20,000–40,000 m⁻² commonly reported (Hunt and Mullineaux 2002), decreasing mortality only by several percentage points would translate to large increases in the harvestable, adult population. One viable strategy is to return clam shell to harvest grounds, thereby buffering muds against the metabolic acids that cause lowered saturation states. Others have suggested shell addition as a viable and important management strategy for oysters and clams, due to the structural complexity shell provides (Gutierrez et al. 2003; Kraeuter et al. 2003; Powell and Klinck 2007). However, shell acting to buffer against dissolution mortality may be at least as important a consequence of this management strategy and could be the primary factor responsible for increased bivalve densities.

Results from the West Bath field experiment support the potential use of shell hash as a means to increase pore-water calcium-carbonate saturation state, and increase recruitment of sediment-dwelling bivalves. Although we increased the average sediment saturation state within retrieved cores from 0.25 ± 0.01 to only 0.53 ± 0.06, numbers of live *M. arenaria* in buffered sediment increased almost three-fold in 2 weeks (Fig. 4). Presumably micro-zones around added shell material exhibited a buffered region with a much higher saturation state than average conditions. Furthermore, Carriker (1961) found much higher settlement densities of juvenile *M. arenaria* in sediments immediately adjacent to discarded shell material. We cannot determine from our data whether sediment buffering decreases post-settlement mortality, acts as a recruitment cue, or some combination of both. Ancillary behavioral observations of juvenile *M. mercenaria* clams migrating towards shell debris in the experimental laboratory cores suggest that buffering may act as a positive recruitment cue. Regardless of mechanisms, returning shell material to clam beds during spawning provides a

management practice to decrease dissolution mortality, as well as increasing other beneficial habitat effects for bivalves (Guitierrez et al. 2003; Kraeuter et al. 2003; Powell and Klinck 2007). Therefore, shell addition to bivalve grounds provides a strategy for enhancing both the ecological (Newell 2004) and economical benefits of increased bivalve populations.

In this study, we show that death by dissolution appears to be an important size-dependent mortality factor for juvenile bivalves. When sediments are moderately undersaturated with respect to aragonite, even when overlying water is supersaturated, significant dissolution mortality of the assemblage occurs. Dissolution of recently set bivalves has profound ecological and commercial implications because large losses of settling bivalves may occur simply as a result of the biogeochemical conditions the bivalves encounter. The role of carbonate saturation state in regulating community structure of carbonate-bearing fauna needs to be addressed. Results from this study suggest that the changes in ocean chemistry as a result of anthropogenic CO₂ injection, coastal eutrophication, and acid rain have the potential to alter existing biological communities. Sediment buffering is one strategy that may help preserve commercially and ecologically important sediment-dwelling bivalves in coastal areas, and certainly merits further investigation.

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