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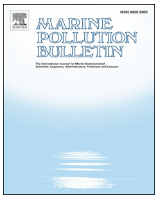

Variability in sediment-water carbonate chemistry and bivalve abundance after bivalve settlement in Long Island Sound, Milford, Connecticut

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ABSTRACT

Cues that drive bivalve settlement and abundance in sediments are not well understood, but recent reports suggest that sediment carbonate chemistry may influence bivalve abundance. In 2013, we conducted field experiments to assess the relationship between porewater sediment carbonate chemistry (pH, alkalinity (A_t), dissolved inorganic carbon (DIC)), grain size, and bivalve abundance throughout the July–September settlement period at two sites in Long Island Sound (LIS), CT. Two dominate bivalves species were present during the study period *Mya arenaria* and *Nucula* spp. Akaike's linear information criterion models, indicated 29% of the total community abundance was predicted by grain size, salinity, and pH. When using 2 weeks of data during the period of peak bivalve settlement, pH and phosphate concentrations accounted 44% of total bivalve community composition and 71% of *Nucula* spp. abundance with pH, phosphate, and silica. These results suggest that sediment carbonate chemistry may influence bivalve abundance in LIS.

1. Introduction

As bivalves transition from pelagic larvae to benthic juveniles, settlement cues are known to aid in substrate selection (Hadfield, 1984; Marinelli and Woodin, 2002; Woodin, 1986; Woodin et al., 1998). On a broad scale, settlement is dependent upon physiochemical properties of habitat (Rhoads, 1973; Sanders, 1958; Weinberg and Whitlatch, 1983), whereas on a local scale, recruitment can be influenced by sediment type (Hunt, 2004; St-Onge and Miron, 2007), organism size (St-Onge and Miron, 2007), and sediment biogeochemistry (i.e., porewater gradients). Decomposition of organic matter may result in steep solute gradients (Thayer, 1983), altering oxygen concentration, ammonia levels, redox potential, and metal and calcite/aragonite saturation state (Burdige, 2006) that can affect infaunal recruitment and survival. These chemical changes at the sediment-water interface may influence the nutritional characteristics and physiological environment of the benthos on a micro-scale of mm to cm (Levin and Edesa, 1997; Marinelli, 1994; Meyers et al., 1987).

Acceptance or rejection of habitat by bivalves is not well understood, but previous studies have examined which factors may contribute to habitat selection and bivalve abundance. Research studies have focused on environmental, chemical, and physical variables at the sediment-water interface which promote settlement and abundance of bivalves. Experiments with *Mercenaria mercenaria* observed an increase in burrowing of juveniles at temperatures ranging from 25 to 30 °C (Savage, 1976). In laboratory experiments, surf clam larvae, *Spisula solidissima*, preferred coarser-grained sandy sediments over finer-grained muddy sediments (Snelgrove et al., 1998). Sediment porewater carbonate chemistry has been linked to larval settlement and survival in life stages of many other marine bivalves (Clements and Hunt, 2014, 2017; Clements et al., 2016; Green et al., 2004; Green et al., 2013). Even after successful site selection, high shellfish morality can occur from micro-scale changes in the chemical composition of sediment geochemistry (i.e., hypoxia, pH changes, and/or carbonate saturation changes), predation, or disease.

During larval development, the initial form of calcium carbonate is amorphous calcium carbonate (ACC), which rapidly develops into aragonite during shell construction (Gazeau et al., 2013). Most bivalves begin benthic existence with an aragonite shell, with the transition from ACC to an aragonite shell occurring before transformation to a motile veliger larva (Harper et al., 1997; Taylor, 1973). Upon reaching adulthood, bivalves either maintain an aragonite shell or shift to a calcite shell or a combination of calcite/aragonite shell, depending upon species. Most adult bivalves have aragonite shells, which has been demonstrated as stronger than calcite, potentially providing greater protection from predation (Green and Aller, 2001; Green et al., 1998).

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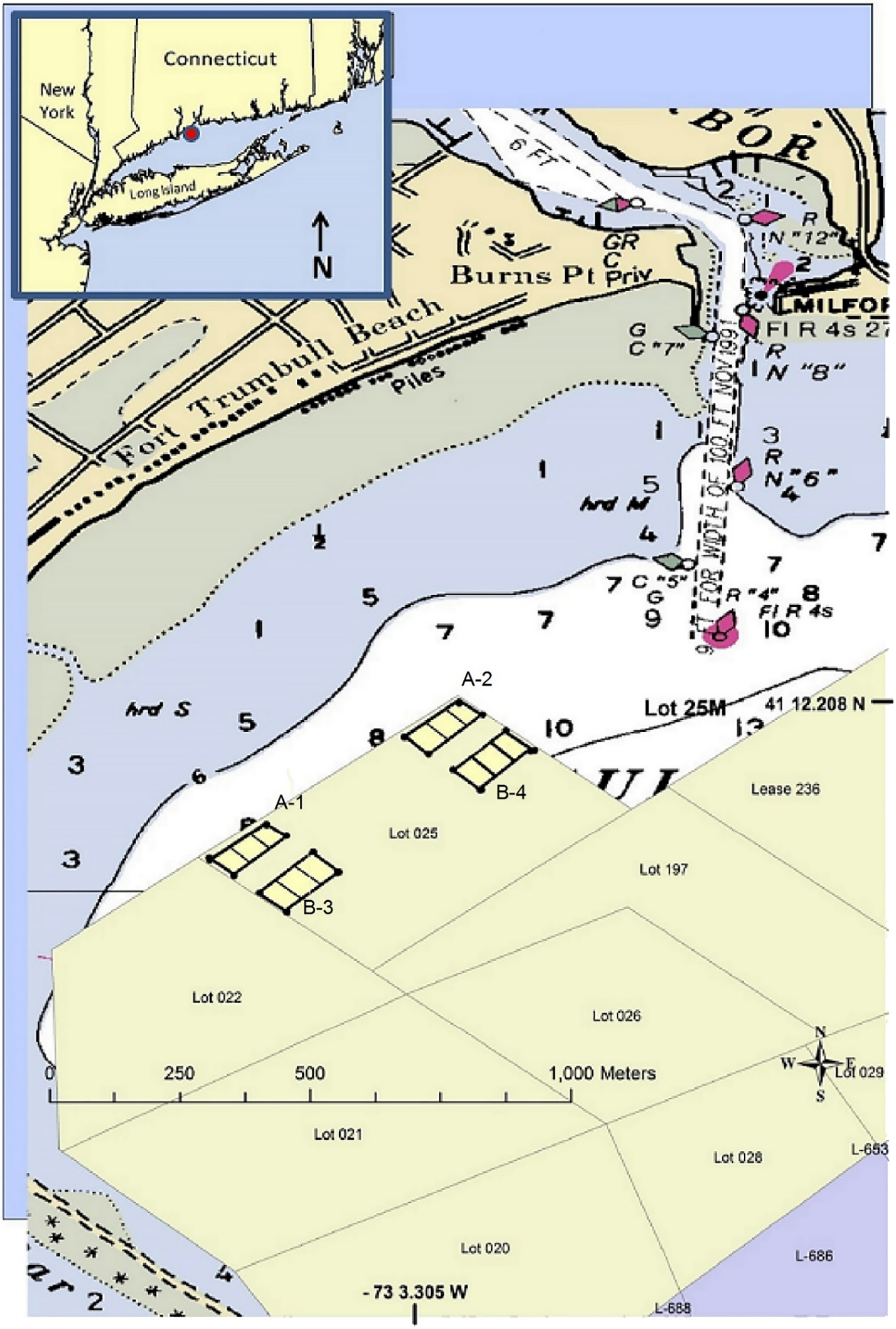

Fig. 1. Map of sampling locations nearshore (A) and offshore (B) within Long Island Sound, CT, USA. Each location contains two nearshore (1-A and 2-A) and farshore (3-B and 4-B) sites. Each site was further divided into three subsets for sampling, indicated by the lines within each plot.

Coastal areas, estuaries, and deltas can be characterized as highly productive areas that receive high inputs of organic and inorganic carbon (Cai et al., 2011; Hedges and Keil, 1995). At the sediment surface, as particulate material settles aerobic and anaerobic reactions, combined with redox processes, result in the production of carbon dioxide (CO_2) in sedimentary porewater. Once CO_2 is produced it reacts with water to form carbonic acid (H_2CO_3), and dissociates into bicarbonate ions (HCO_3^-), carbonate ions (CO_3^{2-}), and hydrogen ions (H^+) resulting in sediment acidification (Green and Aller, 2001; Tang and Kristensen, 2007; Wenzhöfer and Glud, 2004). Corrosive sediments (aragonite, $\Omega < 1$) can reduce successful settlement, recruitment, and abundance in bivalve populations, as low pH conditions typically are confined to the upper millimeters where bivalves settle (Aller, 1982; Green and Aller, 2001; Zwarts and Wanink, 1989).

In many coastal regions along the eastern United States, the sediments are known to be undersaturated with respect to calcium carbonate (Aller, 1982; Green et al., 2009). Research by Green et al. (1993) suggests that loss of benthic foraminifera observed in Long Island Sound (LIS) might correspond to a lack of Ω measured in marine sediments. Laboratory experiments using LIS sediments (41°10.03 N, 72″57.43 W) observed increased mortality of *Nucula annulata* and *Tellina agilis* in undersaturated sediments (Green et al., 1998). Studies which examined effects of sediment acidification on recruitment and dispersal of *M. arenaria* observed greater settlement on sediments with a higher buffering capacity (Clements and Hunt, 2014). Experiments with *M. mercenaria* observed a 10% increase in daily mortality when Ω decreased from 1.6 to 0.6 (Green et al., 2009). At field sites in Maine, "death by dissolution" was observed in bivalve larvae settling in Ω undersaturated sediments, whereas sediment buffered with calcium carbonate showed higher recruitment, possibly a result of favorable pH conditions, decreased mortality, or a combination of the two (Green et al., 2009). Experiments with *Macomona liliana* suggested a link between sediment chemistry and post-settlement behavior, with bivalve settlement decreasing as pH declined (Cummings et al., 2009). Increased sediment acidification may also decrease burrowing behavior for *M. arenaria* (Clements et al., 2017; Clements and Hunt, 2014; Clements et al., 2016). These studies all highlight the importance of sedimentary chemistry for bivalve larval settlement and burrowing.

Low pH (acidified sediments) and undersaturation with respect to carbonate minerals has been documented sporadically in LIS waters during the last three decades (Aller, 1982; Green and Aller, 2001; Green et al., 1993). Further studies are needed to better understand how pH, carbonate chemistry, and other geochemical conditions influence patterns of bivalve settlement and abundance, when other biological activities may result in acidic sediments (Green and Aller, 2001; Green et al., 1998).

In Connecticut, the seafloor is leased to shellfish growers by the state's Department of Agriculture, Bureau of Aquaculture with *M. mercenaria* and *Crassostrea virginica* typically harvested. Many growers rely on natural reseeding of *M. mercenaria* to occur. Understanding the influence that sediment acidification may have on natural settlement, recruitment, and abundance of commercial bivalves is essential to maintain sustainable harvesting of shellfish. To explore relationships between abundance of bivalve molluscs and physical (grain size) and chemical variables (carbonate parameters) at the sediment-water interface, sediments were sampled to assess bivalve community composition and abundance concurrently with carbonate measurements on two adjacent seafloors in LIS. The study was conducted during summer months when bivalves normally settle to the benthos and Ω in LIS tends to be low (Wallace et al., 2014).

2. Materials and methods

2.1. Benthic and grain size sampling

Within the State of Connecticut, due to LIS seafloor being leased for the harvest of shellfish, sampling site selection was based upon the following criteria: (1) permission by shellfish leaseholder to take sediment samples, (2) sediments must not have been harvested recently (> 2 months), and (3) variable sediment grain size between sampled areas. Based upon these criteria, a location in the central basin of LIS (approximately 41°12.0′N latitude and 73°3.0′W longitude; Fig. 1), was identified as the study area. Two sampling locations 10,200 m^2 were vertically located 100 m apart from each other and identified as near-shore (A) and far shore (B). Each sampling location was subdivided into 2 sites (5100 m^2) with near-shore sites identified as 1 and 2, and far-shore sites identified as 3 and 4, and were horizontally separated by 350 m (Fig. 1). For statistical analysis, each site was nested into location due to coastal processes that can influence sediment geochemistry. From each study site (1, 2, 3, and 4) three haphazardly spaced samples ($n = 3$) were taken to ensure that each sampling location was replicated ($n = 6$).

Benthic and chemical field sampling was conducted on 8 occasions aboard NOAA's R/V Victor Loosanoff from July 29 to September 23, 2013 when bivalve abundance typically is greatest (Goldberg et al., 2014) and oxygen concentrations and Ω in LIS tend to be low (Wallace et al., 2014). Benthic and chemical sampling was conducted concurrently so that sediment chemistry could be paired to bivalve abundance.

Bivalve community sampling was conducted using a Smith-McIntyre grab to collect sediments. Sediment grab samples had an approximate surface area of 0.1 m^2. From the corner of the Smith-McIntyre, a 10-cm × 1-cm depth subsample (area = 0.001 m^2, approximately 1% of the total grab) was removed for grain-size analysis. Sediment samples were dried at 60 °C, acid-washed with 1 M hydrochloric acid to remove carbonates, wet-sieved to remove fine sediment (< 63 μm) and dried again at 60 °C. Next, sediment was dry-sieved for 20 min using a Meinzer II sieve shaker into the following size fractions: 1 mm, 500 μm, 250 μm, 125 μm, 63 μm, and < 63 μm (from wet sieving) for classification (Wentworth, 1922). Along with grain-size classification of sediments, sediment porosity and percent shell material through acidification also was determined. Sediment porosity was calculated as the difference between the wet sediment weight and the dry sediment weight. The percent shell material through acidification was calculated as

$$shell(\%) = (DS - ADS)/DS$$

where shell (%) was the percentage of shell material through acidification, DS was the dried sediment weight, and ADS was the dry sediment weight after acidification.

The remainder of the sediment from the Smith-McIntyre grab (approximately 99% of the grab), to a depth of 3.5 cm, was removed to inspect for newly settled bivalves. The material was sieved through a 4-mm screen onto a 500-μm screen. Material was rinsed further with seawater and washed into a jar. Sediment was examined using 10× lighted dissecting microscopes, and all bivalves were removed, counted, and identified to the lowest taxon possible (Gosner, 1978). Environmental data (temperature and salinity) were measured near the sediment-water interface at the beginning and end of each sampling trip by a handheld salinity, conductivity, and temperature meter (YSI 30, Yellow Springs Instrument Co., USA).

Ideally, benthic bivalve abundance, sediment grain size, and sediment chemistry should be performed on the same grab sample to account for geochemical variability that may exist on small spatial time scales. However, logistically the volume of material from the upper few mm of sediments necessary for chemical, benthic, and grain size analysis required that these samples be taken separately. To collect porewater for chemical analysis, sediment cores were obtained using a gravity sediment corer; this sampling device allows recovery of the sediment-water interface and sediment directly beneath, resulting in minimal disturbance to the bottom (Alix et al., 2013; Hongve, 1972). Using the same latitude and longitude from the Smith-McIntyre grabs, four sediment cores were obtained to provide sufficient porewater for chemical analysis. Once core samples were collected, they were transferred to a cooler to preserve porewater chemistry and transported back to the laboratory. To reduce changes in geochemistry, all sediment cores were kept vertical and cold (4 °C) until analyzed, sectioned in a nitrogen filled Erlab 2200 ANM Captair Pyramid Glove Bag, and processed within 2 h of collection to ensure minimal change in sedimentary geochemistry.

2.2. Porewater carbonate chemistry

Before sectioning, both pH and oxygen concentrations were determined using microelectrodes. Porewater pH was measured using a pH -500 electrode (Unisense, Denmark) with an outside diameter and sensitivity length of 400–600 × 400–800 μm, a response time < 10 s and sensitivity of 0.1 pH unit. The pH probe was standardized with pH buffers 4 and 7 (Thermo Scientific™ Orion™ Standard, Waltham, Massachusetts, USA). A TRIS buffer, Batch 9, from Andrew Dickson lab was used to ensure accuracy of the pH probe. Dissolved oxygen concentrations were analyzed using an OX50 probe (Unisense, Denmark) with an outside diameter of 40–60 μm and a detection limit of 0.3 μM. Both probes were attached to a 4-channel microsensor amplifier (Unisense, Denmark) that allowed concurrent measurement of the two variables. A MM33-micro-manipulator was used to manually lower both probes into the sediments. Probes were calibrated prior to use according to manufacturer instructions. After pH and oxygen concentrations were obtained, the upper 1 cm of each core was sectioned, placed in a 50-ml centrifuge tube, and spun at 1000 × g for 10 min to obtain porewater. Next, porewater was filtered by syringe through a 0.45-μm filter with the effluent collected in 15 ml polypropylene tubes. The effluent was placed on ice and held in the dark for subsequent nutrient, DIC, and alkalinity (A_t), determinations. DIC and A_t sample volumes were low (< 10 ml) making preserving with mercury chloride difficult. Therefore these samples were run immediately after collection so preservation with mercury chloride was not required (Dickson et al., 2007; Grasshoff et al., 2009). All analysis was completed within 2 h after cores were sectioned.

Phosphate and silica were quantified with a QuAAtro 39 Continuous Flow Analyzer (Mequon, Wisconsin, USA) following the protocol outlined in methods Q-064-4 for phosphate and Q-066-03 for silica. Briefly, a reduced phosphomolybdenum blue complex was read at 880 nm for phosphate measurements. The method was linear from 0 to 20 μmol kg^{-1}, with a detection limit of 0.01 μmol kg^{-1}. Soluble silicate was measured by a process which reduces the silico-molybdate complex in acid to produce a molybdenum blue complex that is measured at 820 nm, with a linear range between 0 and 130 μmol kg^{-1} and a detection limit of 0.01 μmol kg^{-1}.

A_t was determined spectrometrically (590 nm) by using a weak formic acid to neutralize all basic species and mixing with bromophenol blue (Sarazin et al., 1999). The advantage of this method is that A_t can be determined on small volumes within 1% agreement with classic, Gran's potentiometric titrations. Standards of known A_t were prepared daily to obtain a calibration curve, and certified reference materials (CRM batch 112, 2223.26 ± 0.89 μmol kg^{-1}, A. Dickson, Scripps Institute of Oceanography/University of California San Diego, CA, USA) were run along with the samples to ensure accuracy. All calculated CRM values were within ± 2% of the reported CRM.

Total dissolved inorganic carbon (DIC) was measured with acidification and a LI-COR CO_2 Analyzer (Apollo SciTech, Newark, Delaware, USA). The same CRM batch 112 also was analyzed for accuracy comparison (2011.09 ± 0.47 μmol kg^{-1}). All values were within 0.5% of the certified reference material. All equipment used for carbonate chemistry was part of an international inter-laboratory comparison (Bockmon and Dickson, 2015). Salinity, temperature, pH, phosphate, silicate, A_t, and DIC were entered in CO2SYS (Pierrot et al., 2006) to obtain Ω.

2.3. Statistical analysis

Bivalve and sediment data were analyzed using the statistical software program Statgraphics (Statpoint Technologies, Inc., Warrenton, Virginia). Environmental data and community data were first tested for outliers and then normality using the Shapiro-Wilk test with $p < 0.05$ indicating significance. When the assumption of normality was not met, data were transformed. Phosphate, silica, and Ω were all transformed by log (x) to meet the assumption of normality. Percent shell material was transformed by arcsine (sqrt) for analysis. Bivalve community and individual species also were transformed, and to account for zero values, data was transformed as log (x + 1), where x was the total number of a given bivalve species. Grain size, oxygen, A_t, DIC, and pH met assumptions for normality and were not transformed.

Environmental and benthic data then were analyzed using a nested MANOVA, with date and location (A and B) as fixed factors, and site (1–4, Fig. 1) nested within location. The multiple range test used the Bonferroni correction. For graphical purposes all chemical and biological data were plotted as original values (not transformed) to ensure that concentrations could be observed easily.

The Akaike's information criterion (AIC) was used as the selection criterion to investigate the relationship between environmental conditions and benthic community (Anderson, 2007). As with the MANOVA data, to meet the assumptions of homogeneity, homoscedasticity, and normality the benthic data were transformed log (x + 1) for the model. In an AIC model, parameters that are highly correlated must be excluded from the analysis. Correlations between all independent variables were assessed using multiple variable analysis with Spearman Rank correlation (< 0.60) to determine which environmental variables should be excluded from the AIC model. The Spearman Rank correlation indicated that all carbonate parameters (pH, DIC, and A_t,) correlated with Ω and with DIC and A_t. Therefore, none of the AIC models runs included Ω or DIC with A_t. The model was run in a step-wise manner to provide information about the relationship between environmental conditions and benthic communities. The first model was analyzed to assess how physical properties (grain size, temperature, and salinity) at the sediment interface influenced bivalve abundance. The second step involved the addition of one of the carbonate parameters (pH, DIC, or A_t) to determine which of these factors had the strongest relation with bivalve community. The third step-wise approach was to add the remaining environmental parameters (oxygen, % shell, phosphate, and silica) to the carbonate model (second model) to determine the best correlation among parameters. For example, if pH provided the best correlation for *Nucula* spp., while A_t produced the best fit for *M. arenaria*, then the remaining parameters were added to the carbonate models. By running the AIC model in a step-wise manner, we examined the influence of physical attributes, carbonate characteristics, and other environmental variables on benthic assemblages.

The sampling regime was designed to compare correlations between carbonate chemistry and benthic bivalves for the entire season; however, by using all dates the model may under estimate settlement because of natural changes that can occur over the sampling season (i.e., mortality, grazing). Following a similar procedure as outlined in Clements and Hunt (2018), we addressed these effects by re-running the model using only the first three sampling dates (conducted within 15 days of each other) when highest settlement occurred. These models were run with all the physical, environmental, and the best carbonate parameter (pH, DIC, or A_t) as determined for the models above. By focusing on this narrow window of sampling we attempted to minimize other effects and focus on settlement cues. In addition to the AIC model, another option for removing temporal patterns was utilized. This involved averaging the data from each of the sites (1–4) and using linear regression to assess the relationship between sediment grain size, carbonate chemistry and bivalve abundance.

For all AIC models, the “Best” model fit was determined with the following five criteria: (1) having a low AIC, (2) least number of

Table 1
MANOVA results for physical and chemical sedimentary measurements. The % shell was arcsine (sqrt) transformed, while the phosphate, silica, and Ω was transformed by log. Bold indicates statistically significant *p*-values. The number in () are the degrees of freedom. A_t is for alkalinity, DIC is dissolved inorganic carbon, and Ω is the calculated aragonite saturation state.

	Grain Size	% Shell	pH	Oxygen	Phosphate	Silica	A_t	DIC	Ω
Sampling date (7)									
p	0.07	**< 0.01**	**< 0.01**	**< 0.01**	**< 0.01**	**< 0.01**	**< 0.01**	0.18	**< 0.01**
MS	0.05	4.41	0.90	3.35×10^3	0.32	0.08	4.85×10^5	1.74×10^4	4.72
F	1.98	6.82	5.41	7.32	6.65	7.62	23.80	1.65	5.35
Location (1)									
p	**< 0.01**	**< 0.01**	**< 0.01**	**0.02**	**< 0.01**	**< 0.01**	**< 0.01**	**< 0.01**	**< 0.01**
MS	3.06	9.10	0.11	2.67×10^3	2.90	0.81	1.19×10^5	3.26×10^5	17.7
F	112.57	14.06	0.71	5.83	61.05	79.34	5.86	3.10	20.09
Site (nested in location-1)									
p	**< 0.01**	0.14	**< 0.01**	0.14	**< 0.01**	**< 0.01**	**< 0.01**	**< 0.01**	**< 0.01**
MS	0.97	1.43	3.14	996.69	1.08	0.13	1.75×10^5	1.91×10^5	15.15
F	35.70	2.20	18.91	2.18	22.74	13.12	8.59	18.12	17.14
Sampling date × Location(7)									
p	**< 0.01**	0.85	0.66	**< 0.01**	**0.03**	**0.04**	**< 0.01**	**< 0.01**	0.79
MS	0.08	0.30	0.12	2.26×10^3	0.11	0.02	1.19×10^4	3.26×10^4	0.48
F	2.89	0.65	0.71	4.94	2.31	2.31	5.86	3.10	0.55

variables, (3) highest R^2, (4) similar adjusted R^2 to R^2, and (5) lowest Mallows' C_p The AIC value, R^2, adjusted R^2 and mean square error (MSE), along with the best fit variables, were reported.

3. Results

3.1. Physical sediment characteristics

Grain size was significantly different between locations ($p < 0.01$), but did not vary between dates ($p = 0.07$), and there was an interaction between sampling date and location (< 0.01; Table 1). There was significant variability among sites nested within location ($p < 0.01$). The near-shore locations had a significantly lower mean phi size of 2.89 (fine sand), whereas the far-shore locations had a mean grain size of 3.28 (very fine sand, Fig. 2A).

Location and sampling date each had a significant effect upon percentage of shell in the sediments ($p < 0.01$ and $p < 0.01$; respectively, Table 1). There was no variability between sites nested within location ($p = 0.14$) and no interaction between location and sampling date ($p = 0.85$). The near-shore locations had less shell than the far-shore locations (Fig. 2B). Throughout the season, the % shell decreased for both locations, and there were two homogenous groups (Fig. 2B). At the beginning of sampling, the near-shore locations had 2.9% shell material which decreased by 30% to 2.0% shell material by the end of the season. The far-shore locations had a higher initial concentration of shell material at 3.3% which decreased to 2.7% at the end of the sampling season, a 20% loss of shell material.

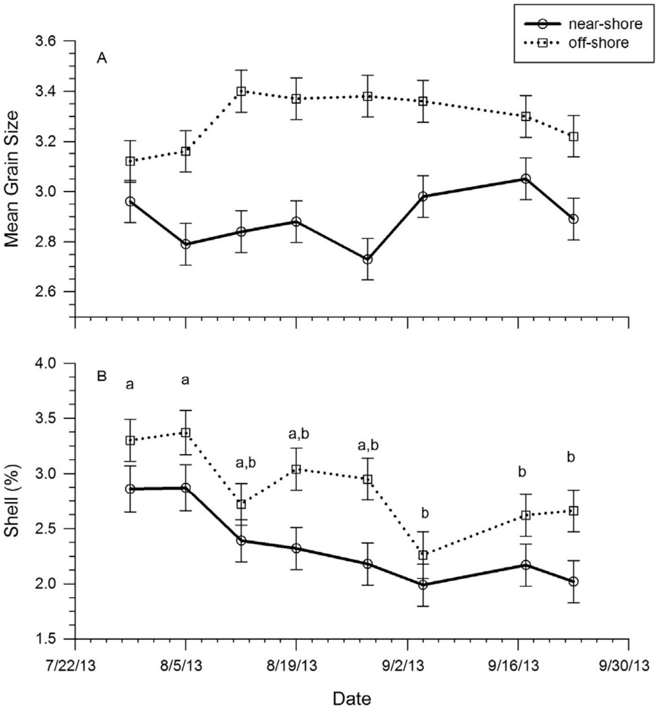

Fig. 2. Mean (± standard error) grain size and percentage of shell in sediments determined through acidification for near-shore and far-shore sites. The letters indicate different homogenous groups for sampling date.

3.2. Molluscan data

Eight bivalve species were identified from sediment samples: the blue mussel (*Mytilus edulis*), common razor clam (*Ensis directus*), dwarf surf clam (*Mulina lateralis*), file yoldia (*Yoldia limatula*), northern quahog (*M. mercenaria*), nutclam (*Nucula* spp.), softshell clam (*M. arenaria*), and transverse ark *(Anadara transversa)*, Data were sufficient to conduct MANOVA analysis on the entire bivalve community and on two of the most-numerous species *Nucula* spp. and *M. arenaria*, which in combination contributed 83% to 100% of the bivalve community identified.

For the community, there were significant effects of sampling location ($p < 0.01$) and sampling date ($p < 0.01$), with no interaction between the two ($p = 0.23$; Table 2). There was variability between sites nested within location ($p < 0.01$). The near-shore locations had fewer bivalves than the far-shore locations (Fig. 3A). For *M. arenaria*, there was a significant difference in sampling date ($p < 0.01$) and location ($p < 0.01$), with variability between sites nested within location ($p < 0.01$), but no interactions between location and date ($p = 0.09$; Table 2). The near-shore locations had fewer *M. arenaria* than the far-shore locations. There were 2 homogenous groups with the number of individuals decreasing throughout the season (Fig. 3B). In the beginning of the season *M. arenaria* represented about 50% of the total species abundance (Fig. 3C). For *Nucula* spp. there was a significant difference between location ($p < 0.01$) but not sampling date ($p = 0.0.09$). There was variability between sites nested within location ($p < 0.01$), but no interaction between the two ($p = 0.90$; Table 2). The near-shore locations had fewer *Nucula* spp. than the far-shore locations, averaging about 40%–60% of the total species abundance throughout the sampling season; in contrast, the far-shore locations

Table 2

MANOVA of total benthic community, *Mya arenaria*, and *Nucula* spp. the two most abundant bivalve species. All data was log (x + 1) transformed for analysis for normality and to account for zeros in the data. Bold indicates statistically significant *p*-values. The number in () is the degree of freedom.

	Bivalve community	*Mya arenaria*	*Nucula* spp.
Sampling date (7)			
p	**< 0.01**	**< 0.01**	0.09
MS	0.87	1.08	0.68
F	3.78	3.70	1.82
Location (1)			
p	**< 0.01**	**< 0.01**	**< 0.01**
MS	31.72	3.83	63.96
F	137.91	13.08	169.97
Site (nested in location-1)			
p	**< 0.01**	**< 0.01**	**< 0.01**
MS	20.44	3.84	56.16
F	130.17	11.28	149.24
Sampling date × Location (7)			
p	0.23	0.09	0.90
MS	0.32	0.54	0.15
F	1.37	1.84	0.40

averaged 60%–80% of the total species abundance (Fig. 3D, E). *Nucula* spp. dominated the total species abundance throughout the sampling period (Fig. 3).

3.3. Porewater chemistry

Both sites had pH values that ranged from 6.18 to 8.34 throughout the season, with the highest pH recorded on August 18, 2013 and the lowest on September 17, 2013 (Fig. 4A). MANOVA identified significant main effects of date for pH ($p < 0.01$), location ($p < 0.01$), and sites nested within location ($p < 0.01$), with no interaction between location and date (0.66; Table 1). There were two homogenous groups for pH (Fig. 4A).

Oxygen concentrations ranged from 168.21 μM to 247.90 μM. There was a significant difference in location ($p = 0.02$) and date ($p < 0.01$) for oxygen. There was no significant difference for site nested within location ($p = 0.14$), but there was an interaction between date and location ($p < 0.01$; Table 1). The near-shore locations had higher oxygen concentrations than the far-shore locations (Fig. 4B). As the season progressed, there was an early August peak in oxygen concentration at both locations, and there were 3 homogenous groups with similar oxygen concentrations at the beginning and end of the season (Fig. 4B).

Phosphate concentrations ranged from 6.22 to 18.79 μmol kg^{-1} with a significant difference between location ($p < 0.01$) and date ($p < 0.01$), with an interaction between the two ($p = 0.03$; Table 1). There was significant variability with sites nested within location ($p < 0.01$). The near-shore locations had lower concentrations of phosphate than the far-shore locations (Fig. 4C). There were 3 homogenous groups, and an apparent seasonal signal, with the highest phosphate concentrations measured in August while concentrations decreased into September (Fig. 4C).

Silica concentrations ranged from 165.50 to 278.11 μmol kg^{-1} with a significant effect of location ($p < 0.01$) and date ($p < 0.01$; Table 2; Fig. 4D). As with phosphate there was significant variability with sites nested within location ($p < 0.01$), and an interaction between location and date ($p = 0.04$). Silica concentrations increased until mid-August then decreased, resulting in 3 homogenous groups.

A_t for the locations ranged from 1635 to 2808 μmol kg^{-1} with the near-shore locations having significantly lower A_t than the far-shore site ($p < 0.01$; Table 1, Fig. 4E). There was a significant main effect of sampling date ($p < 0.01$), and maximal A_t concentrations occurred in August, with 3 homogenous groups (Fig. 4E). There was significant variability with sites nested within location ($p < 0.01$) and an

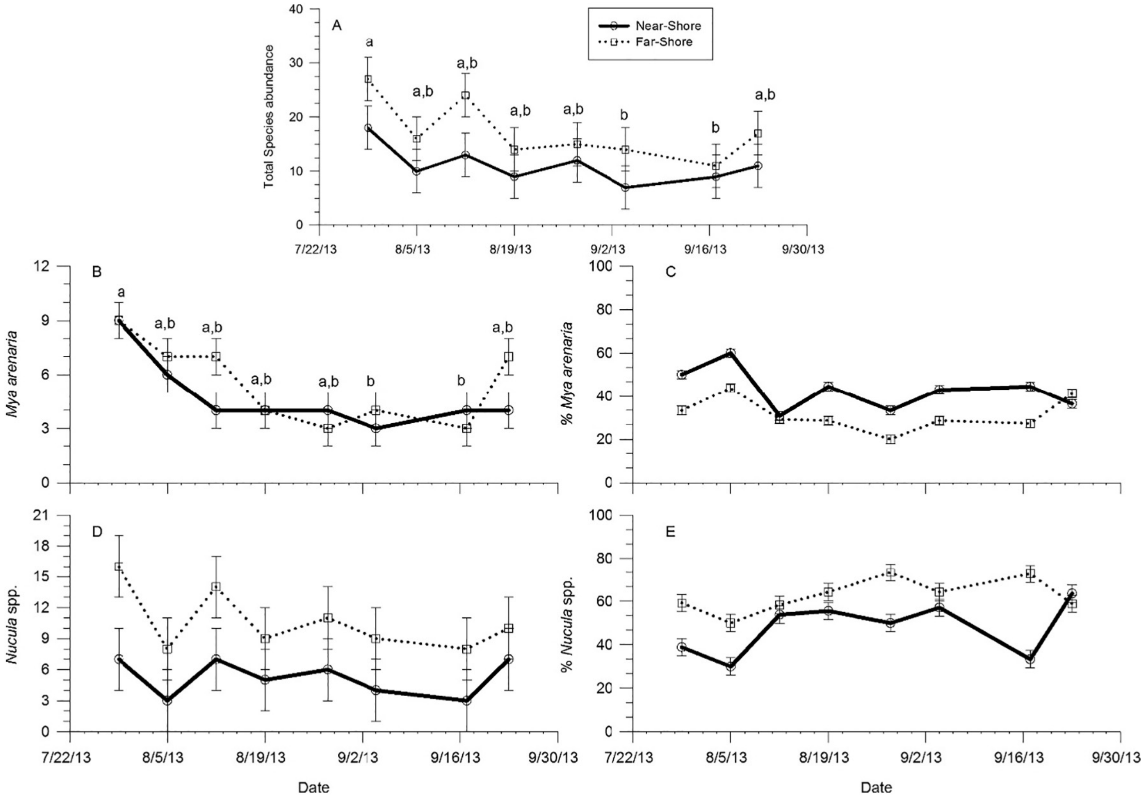

Fig. 3. Mean (± standard error) (A) total bivalve abundance and individual species abundance of (B and C) *Mya arenaria*, (D and E) *Nucula* spp. across sampling dates for near-shore and far-shore sites. The letters indicate different homogenous groups for sampling date.

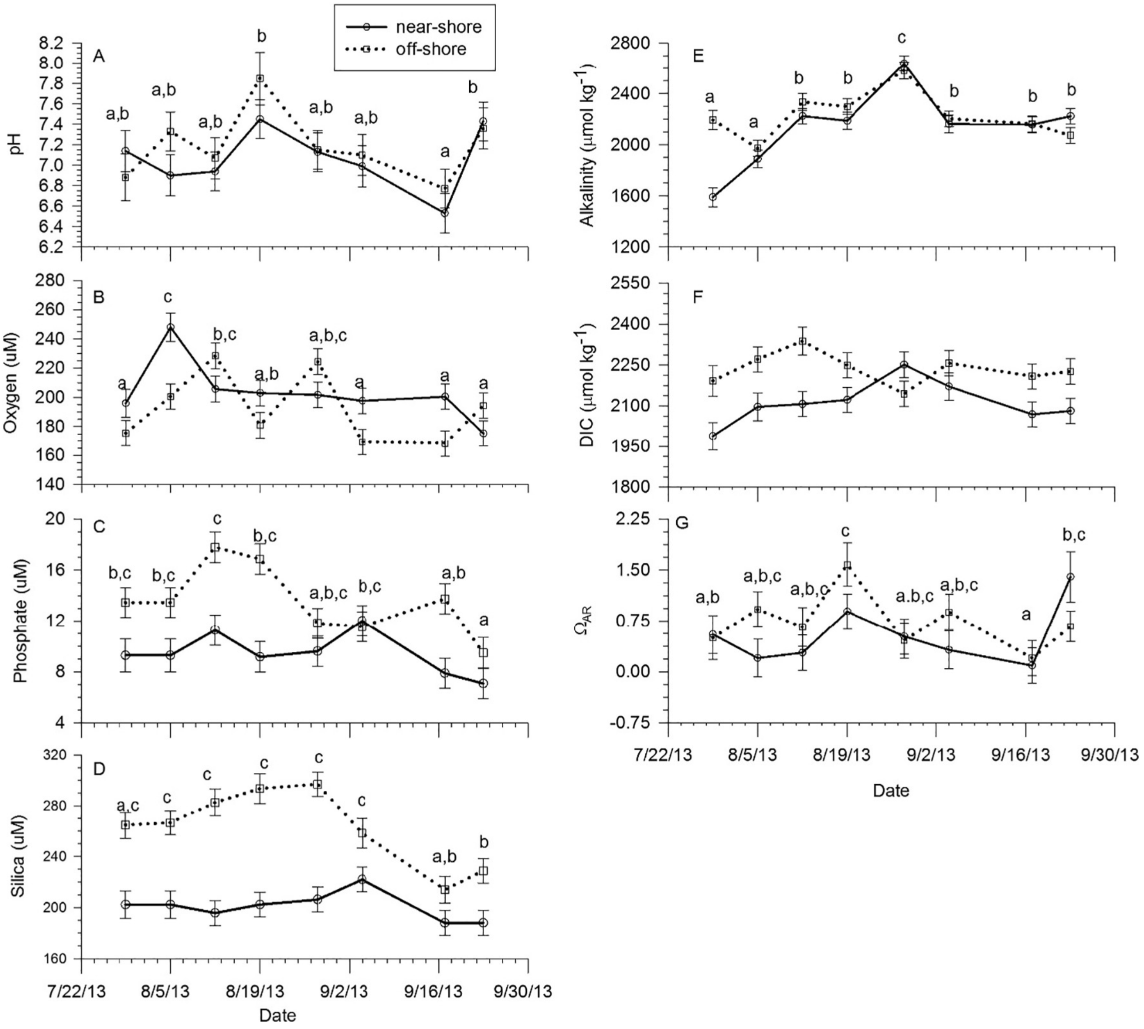

Fig. 4. Mean (± standard error) values are shown for (A) pH, (B) oxygen, (C) phosphate, (D) silica concentrations, (E) alkalinty, (F) DIC, and (G) Ω for near-shore and far-shore sites. The letters indicate different homogenous groups for sampling date.

interaction between treatment and sampling date ($p < 0.01$).

DIC values ranged from 1887.04 μmol kg^{-1} to 2439.16 μmol kg^{-1}. MANOVA results for DIC indicated a significant difference between locations with the near-shore location having lower concentrations of DIC than the far-shore location ($p < 0.01$; Table 1, Fig. 4F), with significant variability with sites nested within location ($p < 0.01$). No significant effect on sampling date was detected ($p = 0.18$), and there was an interaction between sampling date and location ($p < 0.01$; Fig. 4F).

Calculated Ω ranged from 0.30 to 3.52. There was a significant difference between locations ($p < 0.01$), with significant variability between sites nested within location ($p < 0.01$). There was a difference between dates ($p < 0.01$; Table 1). For most of the sampling season, the Ω was below a saturation of 1, with highest concentrations observed in August and September (Fig. 4G), with 3 homogenous groups. There was no interaction between sampling date and site ($p = 0.79$).

3.4. AIC models

With the AIC model, when only physical properties were included in the model, we observed that grain size and salinity explained 25% of the total bivalve community abundance (Table 3). Among the two most abundant species, grain size, temperature, and salinity accounted for 10% of *M. arenaria*, abundance (Table 3), whereas grain size alone accounted for 20% of observed *Nucula* spp. Grain size was an important variable for both species in this model.

When individual carbonate parameters were added to the model (Table 3), the predictability for total bivalve community composition, *M. arenaria*, and *Nucula* spp. increased. When pH alone was added, the predictability of the model increased from 25% to 29% for total bivalve community with grain size, salinity, and pH being the important variables. With DIC or A_t used instead of pH, the model fit did not improve. When pH was added to the model for *M. arenaria* fit increased from 10% to 13%, with grain size, temperature, salinity, and pH explaining the variance; however adding pH did not result in the best fit for *M. arenaria*. The addition of A_t instead of pH or DIC resulted in the best fit at 14%. Similar to the total community results, the best fit for *Nucula* spp. was addition of pH to the model with grain size and pH explaining 30% of the variability and the addition of A_t to the model had the least effect on the population.

Using pH for total community and *Nucula* spp. and A_t for *M. arenaria*, the rest of the geochemical parameters (% shell, oxygen, phosphate, and silica) were added to the model to determine if fit improved. For the total community the addition of % shell resulted in 31% of the total community explained by grain size, pH, and % shell. For *M. arenaria*, addition of more variables did not improve the ability of the model to predict abundance; however, for *Nucula* spp. grain size, pH, and phosphate explained 36% of the observed abundance, a 6% increase in predictability. For both bivalve species grain size was the common variable.

Table 3
Step-wise AIC model results for total community, *Mya arenaria* and *Nucula* spp. The first AIC was run using only physical properties: grain size, salinity (S), and temperature (T). The second model included the physical properties and either pH, dissolved inorganic carbon (DIC), or alkalinity (A_t). The final model included physical, carbonate, and other environmental chemical parameters measured (phosphate, silica, and oxygen). A reduce data set 15 days was analyzed using the final model with all physical, carbonate, and other environmental chemical parameters.

Species	AIC	R^2	Adjusted R^2	MSE	C_p	Variables
Model with physical properties						
Total Community	−0.95	0.25	0.23	0.36	2.17	Grain Size, S
Mya arenaria	−1.17	0.10	0.07	0.28	4.0	Grain Size, T, S
Nucula spp.	−0.10	0.20	0.19	0.86	0.94	Grain Size
Model with carbonate properties						
pH						
Total Community	−1.02	0.29	0.26	0.33	3.18	Grain Size, S, pH
Mya arenaria	−1.23	0.13	0.09	0.26	5.0	Grain Size, T, S, pH
Nucula spp.	−0.22	0.30	0.28	0.75	1.78	Grain Size, pH
DIC						
Total Community	−1.00	0.27	0.24	0.34	3.63	Grain Size, S
Mya arenaria	−1.24	0.13	0.09	0.26	5.0	Grain Size, T, S, DIC
Nucula spp.	−0.16	0.26	0.25	0.80	1.20	Gran Size, DIC
A_t						
Total Community	−0.98	0.25	0.23	0.35	2.18	Grain Size, S
Mya arenaria	−1.25	0.14	0.10	0.25	5.0	Grain Size, T, S, A_t
Nucula spp.	−0.13	0.24	0.22	0.82	1.40	Grain Size, A_t
Model with all environmental parameters						
Total Community	−1.03	0.31	0.28	0.32	0.93	Grain Size, pH, % Shell
Mya arenaria	−1.24	0.14	0.10	0.25	1.60	Grain Size, T, S, A_t
Nucula spp.	−0.26	0.36	0.33	0.69	1.30	Grain Size, pH, phosphate
First 3 sampling dates						
Total Community	−0.68	0.44	0.35	0.35	1.27	pH, phosphate
Mya arenaria	−1.29	0.33	0.22	0.18	−0.89	A_t, phosphate
Nucula spp.	−0.34	0.71	0.64	0.43	1.80	pH, phosphate, silica

When using only the first 15 days of sampling in model simulations, AIC indicated that 44% of community abundance could be accounted for by pH and phosphate (Table 3). With this reduced data set, 33% of *M. arenaria* abundance was observed to be a function of A_t and phosphate concentrations, while for *Nucula* spp. 71% abundance was accounted for by pH, phosphate and silica (Table 3). For the reduced data set, grain size was no longer an important variable, and total bivalve community and both species had a carbonate parameter and phosphate that influenced bivalve abundance.

Linear regression of the data averaged across each site to obtain site means resulted in grain size correlating well with total bivalve community abundance (Fig. 5A), *M. arenaria* (Fig. 5C), and *Nucula* spp. (Fig. 5E) but the relationship was not significant ($p = 0.25$, $p = 0.29$, and $p = 0.25$, respectively). For total bivalve community and *Nucula* spp. there was a significant correlation ($p = 0.03$ and $p = 0.03$) between abundance and pH (Fig. 5B and F). For *M. arenaria* there was a significant correlation ($p = 0.03$) with A_t (Fig. 5D). For both species a carbonate parameter was significantly correlated with abundance. Grain size was plotted versus pH and A_t (Fig. 5G and H, respectively) but even though the correlation coefficient was high it was not statistically significant ($p = 0.21$ and $p = 0.15$).

4. Discussion

Shallow-inshore estuaries, like LIS, are environments that experience chemical and physical fluctuations at the sediment-water interface throughout the season that may influence bivalve settlement and recruitment (Duarte et al., 2013; Waldbusser et al., 2013; Waldbusser and Salisbury, 2014). Numerous studies have demonstrated that water column acidity and Ω can influence survival and growth of various marine organisms (Bach et al., 2017; Bermúdez et al., 2016; Dutkiewicz et al., 2015; Pansch et al., 2012); however, only a few studies have examined in situ sediment acidification in concert with benthic communities (Clements and Hunt, 2018; Green et al., 1993, 1998). Our study documented temporal and spatial variability on a biweekly and monthly timescale of carbonate chemistry in LIS sediments (Fig. 4). We observed that abundance of bivalve communities varied between location (*Nucula* spp.) and over time (*M. arenaria*; Fig. 3). This high spatial and temporal variability in bivalve settlement was consistent with previous research (Clements and Hunt, 2017, 2018; Emerson and Grant, 1991; LeBlanc and Miron, 2006; Möller and Rosenberg, 1983). Our results confirm that, in LIS, there is high spatial and temporal variability with respect to carbonate chemistry and sediment acidification in marine sediments, and on a short-term (2 month) time scale this variability is reflected in bivalve settlement. Long-term studies across seasons and over years are still needed to assess seasonal and yearly variability and how this influences bivalve settlement and abundance.

Many factors can contribute to high variability in bivalve community composition and settlement. The AIC model, including all environmental parameters, accounted for 31% of the total community abundance with grain size, pH, and % shell (Table 3). By focusing on the most prevalent species, the linear models suggested that *M. arenaria* abundance was influenced by grain size, temperature, salinity and A_t, whereas *Nucula* spp. was influenced by grain size, pH, and phosphate. For the community and both dominant species, it appears that carbonate chemistry influenced abundance; however, the contributing carbonate variables were not consistent among species. A relationship between carbonate chemistry and bivalve settlement has been observed in the laboratory with a decrease in burrowing from 60 to 80% (pH = 7.5) to 30–40% (pH = 7.0) for *M. arenaria* (Clements and Hunt, 2014; Clements et al., 2016). Green et al. (2009) studied controlled shell buffering in sediments and observed more juvenile *M. arenaria* settlement in buffered sediment (pH ~7.3) relative to sediments without shell buffering (pH ~7.0). This study, combined with previous research, highlights the importance of sediment pore water carbonate chemistry for bivalve settlement.

Model results also indicated that grain size influenced bivalve settlement (Table 3). This is consistent with laboratory studies that observed both settlement and burrowing behavior to be influenced by grain size (Snelgrove et al., 1998; St-Onge and Miron, 2007). The model suggests that carbonate chemistry and grain size are working in combination to influence bivalve benthic community composition and abundance. Larger grain size allows water to penetrate more easily into sediments, which can result in increased diffusion between porewater and overlying water (Berner, 1980). Measuring grain size with corresponding pH revealed that, although grain size remained unchanged at a given site (Fig. 2), carbonate chemistry variables still affected bivalve abundance (Table 3). There was a correlation between grain size and carbonate parameters but the relationship was not significant (Fig. 5). These data suggest sediment carbonate chemistry and grain size that may exert an effect upon bivalve settlement and abundance. Field experiment using buffered and unbuffered sediment at multiple sites with different grain sizes would provide more detail on the interaction between grain sizes and carbonate chemistry as settlement cues.

By focusing on a narrow range of settlement (15 days), any temporal effects on settlement were reduced. When the AIC parameters were narrowed, the model accounted for 44% of the total benthic

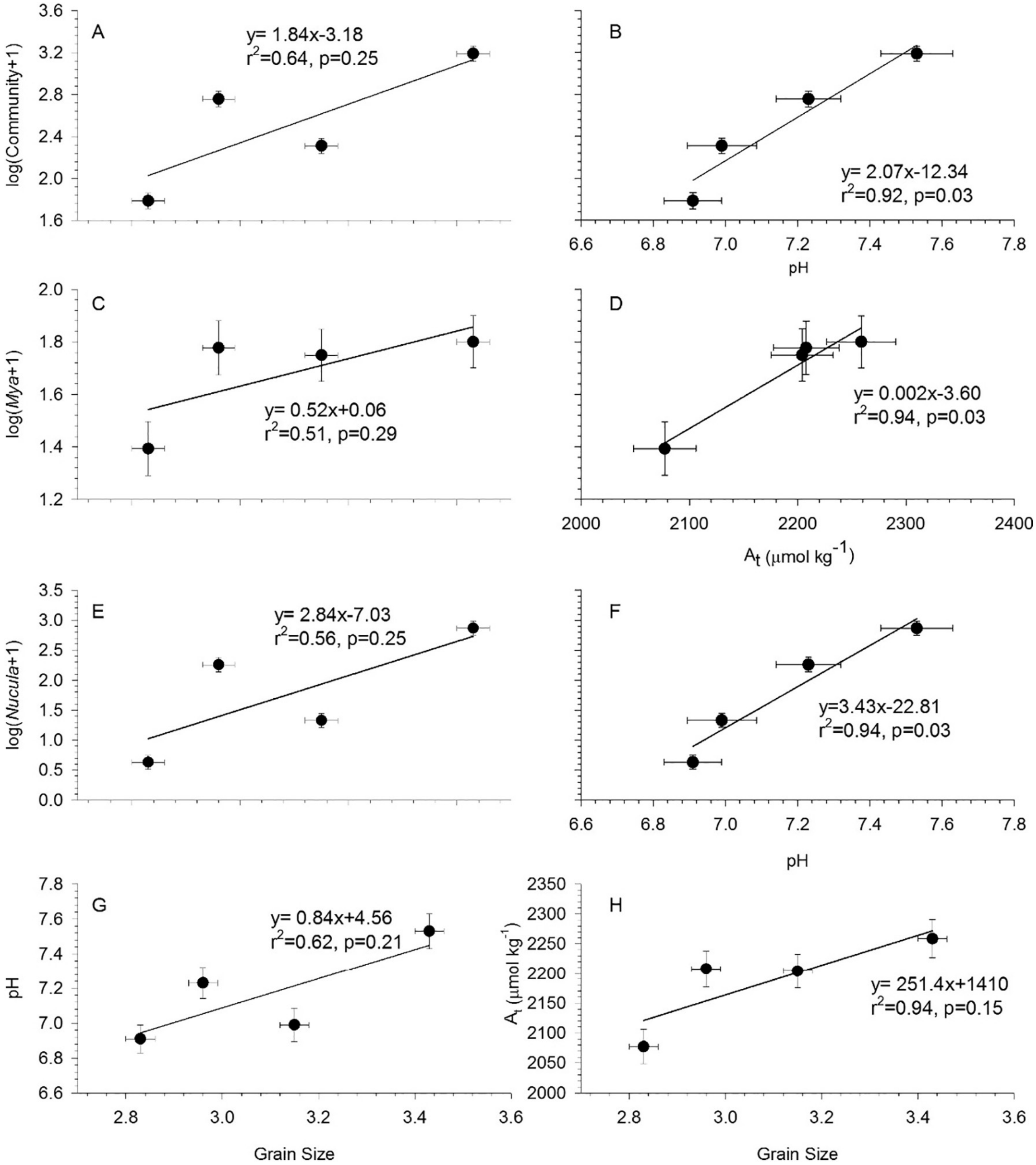

Fig. 5. Mean values (± standard error) for community abundance versus grain size (A) and pH (B), *Mya arenaria* versus grain size (C) and pH (D), *Nucula* spp. versus grain size (E) and pH (F), and grain size versus pH (G) and alkalinity (H) for all dates from each site. Linear correlation r^2 and *p* values were reported for each figure.

community, including 33% of *M. arenaria* and 71% of *Nucula* spp. (Table 3). Carbonate chemistry, with respect to pH for total community and *Nucula* spp. and A_t for *M. arenaria* was still dominant in the model, but grain size was no longer a significant contributor. Surprisingly, phosphate concentrations increased predictability in the model for total community and both species, which was not the case when the entire data set was considered. Although the exact mechanisms of calcium carbonate formation still are being studied, there is strong evidence from crustaceans and bivalves (Addadi et al., 2003) that amorphous calcium carbonate (ACC) or amorphous carbonate phosphate (ACP) are precursors to formation of aragonite (Becker et al., 2005; Lowenstam and Weiner, 1985; Weiss et al., 2002). Research suggest multiple mechanisms in which phosphate may be needed for shell formation: (1) in cooperation with ACC formation or (2) direct ACP inclusion in the shell. Using in vitro experiments, researchers observed that precipitation of ACC required addition of phosphate-containing molecules (Bentov et al., 2010; Clarkson et al., 1992; Xu et al., 2005). Furthermore, RAMAN spectra scanning of ACC shells, shows amounts of phosphate incorporated for in vitro experiments (Bentov et al., 2010). Further scanning of 9-day-old *M. mercenaria* shell determined small amounts of ACP within the overall ACC shell (Addadi et al., 2003). These studies have suggested that the role of phosphate in the ACC structure can be attributed to inorganic phosphate as ACP (Bentov et al., 2010; Gower, 2008; Veis et al., 1991; Weiner et al., 2003). This research has led to the suggestion that inorganic phosphate functions in a cooperative role to form ACC in marine bivalves. In our study examining short time scales, for both bivalve species, carbonate chemistry combined with phosphate concentrations improved predictability, suggesting the role it plays in larval settlement in natural environments may be relevant.

Surprisingly silica was an important variable predicting *Nucula* spp. abundance during the first 3 sampling dates (Table 3). Silica-carbonate replacement in bivalves has been attributed to bulk dissolution or silicification controlled by the force of crystallization (Klein and Walter, 1995; Maliva and Siever, 1988). Laboratory-based experiments at varying temperatures with different concentration of carbonate minerals suggested that silica uptake onto calcite surfaces was irreversible and strongly pH dependent (Klein and Walter, 1995). The interaction of calcium carbonate with silica is still not well understood (Klein and Walter, 1995; Liesegang et al., 2017; Schmitt and Boyd, 1981). Recently Liesegang et al. (2017) used analytical results and a schematic model to demonstrate a coupled dissolution-precipitation mechanisms between calcite dissolution and silica deposition, with calcite dissolution initiating silica precipitation. Their research also indicated that as dissolution was occurring a sharp localized rise in pH and salinity occurred, which induced silica precipitation. The AIC model had silica as an important variable for *Nucula*, suggesting that there might have been some coupled dissolution-precipitation occurring, however this was outside the scope of this project. Further research in understanding how this process may be affecting current bivalve populations needs to be explored.

Previous research in LIS reported increased mortality of bivalves (*N. annulata* and *Tellina agilis*) in sediments that were undersaturated ($\Omega < 1$) with respect to carbonate (Green et al., 1993, 1998). Our study did not focus on determining whether mortality or dissolution was occurring because of undersaturated sediments, however mean Ω values in LIS were undersaturated during most of the sampling season. Higher concentrations of Ω are known to encourage settlement of calcifying organisms and reduce mortality (Green et al., 2009; Waldbusser et al., 2013). In field experiments in Maine (Portland Harbor), sediment buffered with shell material supported higher settlement and decreased mortality of *M. arenaria*, which was attributed to increased carbonate saturation (Green et al., 2009). Depressed burrowing behavior was reported for juvenile *M. arenaria* (Clements and Hunt, 2014; Clements et al., 2016) and adult *Ruditapes philippinarum* (Rodríguez-Romero et al., 2014) in acidified sediments. Using $GABA_A$ receptors, bivalves can avoid acidic sediments that can persist in estuarine environments that are highly dynamic (Clements et al., 2017). Our modeling results suggest that increase pH and A_t may enhance bivalve community recruitment. Bivalve community abundance declined later in the season, perhaps responding to acidic sediments, however, we are unable to discern whether decreased abundance of bivalves that occurred as sediments became more acid was due to dissolution of carbonate, avoidance behavior by bivalves, predation, or a combination of these processes.

For individual species, carbonate chemistry was a common variable in model strength. This is not surprising as all of these species have aragonite shells (Clements and Hunt, 2014; Degens and Spencer, 1966). Previous work in LIS, conducted near our study site, observed sediment grain size to be the best sediment predictor variable for molluscan abundance (Goldberg et al., 2012; Meseck et al., 2014); however, in those studies, carbonate chemistry was not measured and regressions accounted for only 14–18% of variance. In our study, measuring carbonate chemistry doubled the predictability of bivalve abundance. Our results suggest that these carbonate chemistry variables may be helpful in predicting whether or not an environment will be suitable for bivalve settlement.

A number of carbonate chemistry variables correlated well with one another (pH, DIC, A_t, and Ω). We measured pH, DIC, and A_t to determine if one individual carbonate measurement can be used to predict bivalve abundance, and we observed that for the total community and *Nucula* spp., pH increased the model predictability. For *M. arenaria*, A_t was a slightly better predictor than pH. In other studies, Green et al. (2004, 2009) observed that low Ω concentrations resulted in shell dissolution and reduced growth, whereas Clements and Hunt (2017) showed a high correlation between pH and clam abundance (70%). The latter study acknowledged that pH was measured as a proxy for carbonate geochemistry and suggest that other specific carbonate variables may be responsible for differences in bivalve abundance observed. Our study highlights the complex relationship between sediment acidification and benthic bivalve abundance with different carbonate chemistry variables influencing specific benthic bivalve assemblages.

In conclusion, this study suggests that bivalve abundance in LIS may be influenced by small-scale spatial differences in carbonate geochemistry and grain size. The results in this study are based upon model calculations of the observed data and lack some observations of other factors that may influence abundance. For example, predation was not measured in this study and is known to play a major role in recruitment and survival (Beukema and Dekker, 2014; Glaspie et al., 2017; Wilson, 1990). Future studies, measuring predation, carbonate chemistry, and grain size within a season would provide useful information to managers concerning how these natural environmental variations are influencing bivalve abundance.

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