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## Chemistry of surface waters: Distinguishing fine-scale differences in sea grass habitats of Chesapeake Bay

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### *Abstract*

We tested the hypothesis that the physical and chemical processes acting in sea grass habitats of the lower Chesapeake Bay are spatially structured and that dissolved elemental chemistry of sea grass-habitat surface waters have their own unique identity. We sampled surface waters from July to September 2001 in five sea grass habitats of the lower bay: Potomac, Rappahannock, York, Island (Tangier-Bloodsworth), and Eastern Shore. Dissolved Mg, Mn, Sr, and Ba concentrations were measured by sector field inductively coupled plasma-mass spectrometry. As expected, Mg, Sr, and Ba exhibited conservative behavior, but Mn exhibited nonconservative behavior along the salinity gradient. Spatial differences in the chemistry of surface waters over sea grass habitats were fully resolvable independently of time. Moreover, classification accuracy of water samples was low in Rappahannock, moderate in Potomac and Eastern Shore, and high in the York and Island habitats. The chemistry of York was distinct because of the effects of physical mixing, whereas Island chemistry was unique, potentially because of the influence of Coriolis acceleration and river discharges from the Susquehanna River. The results of this study show that sites so close to one another in physical space maintain distinct chemical differences.

Many studies have shown that coastal ecosystems, such as estuaries, are characterized by large-scale spatial and temporal variability in terms of water quality parameters such as temperature, salinity, turbidity, and elemental chemistry. Livingston (1984) argued that slight water quality changes due to pollution, which are outside of the evolutionary experience of organisms, can cause alterations of habitat structure, energy, and species composition of estuarine communities. Macfarlane and Booth (2001) believed that physical and chemical differences that occurred naturally in sediments were the most important determinants in species assemblages among sites in the estuarine reaches of the Hawkesbury River in Australia. Most aquatic ecologists have focused on identifying sources and sinks of contami-

nants (e.g., Coakley and Poulton 1993) or on assessing the impact of pollutants on habitats and organisms (e.g., Stronkhorst 1992). However, we know little about fine-scale differences in water chemistry and their potential role in structuring estuarine communities, the distribution of vegetation, and the population dynamics of estuarine organisms.

In the large scale, dissolved major, minor, and trace-element concentrations, as well as relative abundances of these elements in estuaries, are controlled by a combination of physical and chemical processes that interact to regulate the transmission of dissolved and particulate elements from river to ocean (Paucot and Wollast 1997; Guieu et al. 1998). In estuaries these two broadly defined processes lead to longitudinal (along estuary) variability in the dissolved elemental concentrations along the salinity gradient. Aside from salinity, relative abundances of dissolved elements are affected by physical mixing of fluvial and marine particulates that usually results in the adsorption-desorption of metals and consequent changes in concentration in the dissolved load (e.g., Zwolsman and van Eck 1999; Hatje et al. 2003). In the estuarine mixing zone, increased salinity causes flocculation of river colloids and fractionation of trace elements (e.g., Powell et al. 1996; Wen et al. 1999). Removal of these elements from the dissolved load is also influenced by biological activity (Zwolsman and van Eck 1999; Nozaki et al. 2001). During the spring bloom, the particulate concentration of allochthonous major and trace elements may decrease, whereas the concentration of autochthonous major and trace elements may increase (Zwolsman and van Eck 1999). For example, in the Scheldt estuary, Zwolsman and van Eck (1999) observed that the spring bloom caused increased Ba in suspended matter, otherwise Ba decreased with increasing salinity. Remobilization of trace elements from particulate matter and sediments is also an important mech-

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anism affecting the dissolved chemistry of surface waters in estuaries. Seasonal anoxia, for example, causes reduction and release of trace elements from surface sediments. Processes of remobilization may interact with mixing, leading to complex dynamics in the distribution of trace elements in the dissolved load along the salinity gradient (e.g., Eaton 1979; Paucot and Wollast 1997).

Despite our understanding of the large-scale processes acting in estuaries and their impact on dissolved chemistry, we know comparatively little about the spatial and temporal variability of major, minor, and trace elements across estuaries. In small and narrow estuaries, rapid cross sectional mixing may lead to negligible lateral (across estuary) differences in both salinity and the concentration of minor and trace elements (Smith 1977). However, in large estuaries significant lateral variability in the salinity gradient may occur because of the relative influence of freshwater outflow and oceanic water inflow. Many studies depict lateral heterogeneity in water density either due to Coriolis acceleration (Pritchard 1952; Austin 2004) or to interactions among barotropic forcing, baroclinic forcing, and bathymetry (Huzzey 1988; Huzzey and Brubaker 1988; Valle-Levinson and Lwiza 1995). For example, in a wide estuary such as the Chesapeake Bay, the Earth's rotation may lead to modification of the two-layer estuarine circulation by confining mean outflow of freshwater to the West and mean inflow of oceanic water to the East (Pritchard 1952; Austin 2004). Conversely, bathymetry can influence pressure and density gradients, leading to near-surface convergence flow over channels of the Chesapeake Bay (Huzzey and Brubaker 1988; Valle-Levinson and Lwiza 1995). In systems such as the Chesapeake Bay, it is likely that the density and momentum differences between water masses prevent the lateral transfer of elements across the estuary (Shumilin et al. 1993). Inefficient mixing produces lateral heterogeneity in dissolved element chemistry. Whether such physical structure leads to significant fine-scale spatial differences in the dissolved element chemistry in estuaries such as Chesapeake Bay has not, to our knowledge, been tested. Past studies of estuarine dissolved element chemistry were based on small sample sizes (Zwolsman and van Eck 1999). Small sample sizes may result in low statistical power preventing the resolution of spatial and temporal differences across estuaries. Many investigators have also assumed that there is little temporal variation in estuarine chemistry, and they have collected samples at one point of time to represent a considerably longer period of time. In addition, those that sample over time usually do so at one location, which may not be representative of the entire estuary. Moreover, in wide estuaries such as Chesapeake Bay, studies have focused on the chemistry of the deeper waters (channels) with little attention paid to the chemistry of shallower surface waters (e.g., Eaton 1979; Gavis and Grant 1986; Coffey et al. 1997). Scientists have not attended to the use of surface water elements as geochemical markers that could be used to understand the dynamics and life history of vagile estuarine and estuarine-dependent organisms.

Here we present the results of a study that tested the hypothesis that physical and geochemical processes acting in sea grass habitats of the Chesapeake Bay are spatially structured and that sea grass habitats have their own unique

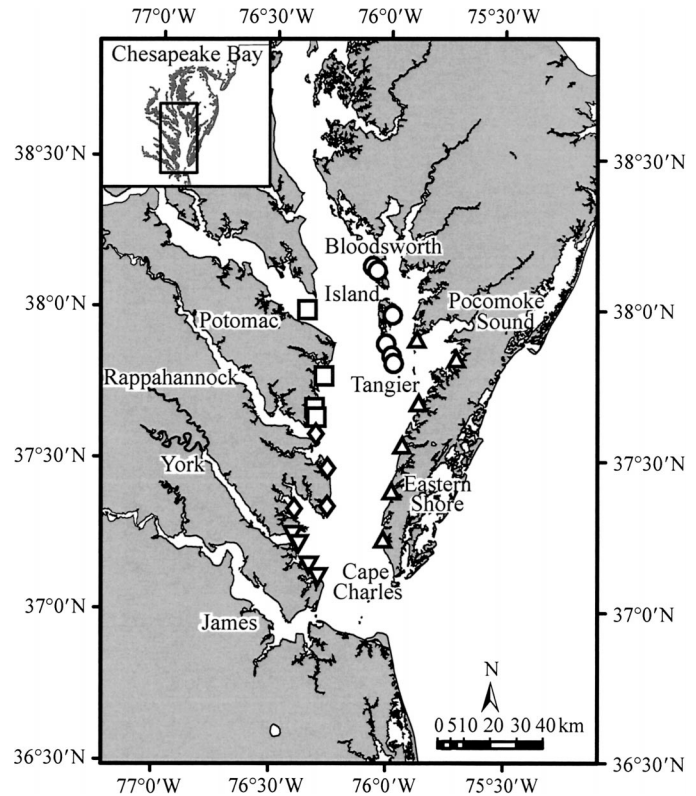


Fig. 1. Map of the Chesapeake Bay showing the location of sampling habitats and stations. Five sea grass habitats were sampled for water: Potomac, Rappahannock, York, Island, and Eastern Shore. At each station water samples were collected twice monthly during spring tides from July to September 2001.

chemical identity. Under our hypothesis, we show that the relative abundances of dissolved elements in surface waters collected from these habitats are spatially resolvable, allowing the identification of most sea grass beds based solely on water chemistry. Support for this hypothesis would be the first unequivocal evidence that fine-scale chemical differences in surface waters can play an important role in structuring estuarine communities, influencing the distribution and extent of vegetation, and determining structure in estuarine and estuarine-dependent biota. Moreover, the demonstration of fine-scale chemical heterogeneity will impact a number of research studies, such as those that use water chemistry as a tool to study Chesapeake Bay-wide processes whether physical or biological. For example, in the case of biological processes, these fine-scale differences would be particularly important in the reconstruction of environmental histories of fish that rely on otolith chemistry.

**Study area**—Chesapeake Bay is the largest estuary in the United States (Fig. 1). Five major tributaries supply most of the freshwater input: the Susquehanna, Potomac, Rappahannock, York, and James Rivers. The mean flow of freshwater in the estuary is approximately  $2,280 \text{ m}^3 \text{ s}^{-1}$  (Austin 2004). The Susquehanna, the Potomac, and the James Rivers contribute 80% of the total freshwater input (Valle-Levinson et al. 2001). The watersheds draining into the Chesapeake Bay

are underlain by four major bedrock types: carbonate rock (limestone, dolomite, marble); crystalline rocks (schist, granite, quartzite, gneiss); siliciclastic sedimentary rock (sandstone, siltstone, shale, conglomerates); and unconsolidated sediments (sand and gravel). The physical and chemical characteristics of the bay are thus strongly influenced by the hydrogeological and geochemical diversity of freshwater sources (Skrabal 1995).

The bay has a very complex bathymetry comprised of natural and navigational channels and shoals. Based on its bathymetry, the bay can be divided into two regions. The deeper upper bay, north of the Potomac River, can be considered an estuary of the Susquehanna River, with this river accounting for up to 87% of total freshwater discharge into the upper bay (Sholkovitz and Elderfield 1988). The second region is the shallower lower bay, from the Potomac River to the mouth of the estuary, with an average depth of 10 m (Valle-Levinson and Lwiza 1995) and with freshwater delivered to the lower bay by the Potomac, James, York, and Rappahannock Rivers.

## Methods

*Sampling design and site selection*—This study focuses on the shallow waters of the lower Chesapeake Bay between 37°00' and 38°20' latitude, an area historically dominated by sea grass beds (Moore et al. 2000). These sea grasses provide critical nursery habitat for larval and juvenile fish, mollusks, and crustaceans. Based on the physical characteristics of these sea grass beds and their spatial distribution, we divided the lower bay into five major habitats (Fig. 1):

- (1) Potomac habitat: mouth of the Potomac River to the northern shore of the Rappahannock River.
- (2) Rappahannock habitat: mouth of the Rappahannock River to the northern shore of the York River.
- (3) York habitat: mouth of the York River to the northern shore of the James River.
- (4) Island habitat: Tangier Island to Bloodworth Island.
- (5) Eastern Shore habitat: Pocomoke Sound to Cape Charles.

In each habitat, six spatially fixed stations were established along the salinity gradient. In the Potomac, the Rappahannock, and the York habitats three of the six stations were located in the river mouths. We accessed stations using a 21-ft. fiberglass boat, and at each station samples were collected twice monthly, during spring tide from July through September 2001. During spring tide, mixing was maximized in the water column (Valle-Levinson et al. 2000), and we therefore assumed that surface water mixing was at its maximum across the estuary. Therefore any spatial differences in chemistry among sea grass habitats reflected minimal differences compared to neap tide conditions.

*Water collection*—Water was collected in a quasi-synoptic fashion over 4 d. In general, it took 1 d each to sample the Island and Eastern Shore habitats and 2 d to sample the three Western Shore habitats. Within a given habitat all samples were collected in the same day and over different tidal phases. Thus seasonal samples from a given habitat reflected the

variability in dissolved chemistry attributable to the effect of location.

At each station, water was collected at a randomly selected site using clean-method procedures (Sholkovitz and Elderfield 1988; Powell et al. 1996 with some modifications). Each sample was pumped at 50 cm depth using a peristaltic pump (Masterflex 7520-60) and acid-washed Teflon tubing. The tubing was maintained at depth using a glass probe weight. While being pumped, water was filtered through a certified Gelman capsule (GWV, 0.45  $\mu\text{m}$  Versapor) to exclude the particulate fraction but retain the colloidal and dissolved fractions. So, in this study we analyzed the sum of the colloidal and dissolved fractions and operationally defined these measurements as total dissolved element concentration. During the first 10 min of pumping, water was not sampled, allowing 4–5 sample volumes to purge the system. Thereafter, water was collected in acid-washed high-density fluorinated Nalgene bottles (250 ml) and acidified to pH < 2 using 1 ml of ultrapure  $\text{HNO}_3$ . After sampling, the filtration system was again allowed to flush completely. Each filter was used to collect four to six samples within habitat only. Sholkovitz and Elderfield (1988) observed no sampling artifacts in water samples collected similarly along the salinity gradient in Chesapeake Bay. All sample bottles were stored in double Zip-loc bags, chilled on ice in the field, and refrigerated in the laboratory until analysis.

During water sampling, we also measured temperature, salinity, conductivity, pH (YSI 63), dissolved oxygen (DO; YSI 55), and depth. The phase of the tide was noted. For continuous, long-term temperature and salinity monitoring, we used HOBO sensors (Onset U.S. Patent 5373346) and microcat-seabird thermosalinographs (SBE 37).

*Water analysis*—Water samples were prepared for analysis in a class-100 clean room, and elements were analyzed using external calibration with internal standardization (Indium; Taylor 2001). Water samples were diluted fivefold by spiking a subsample of 200  $\mu\text{l}$  with 800  $\mu\text{l}$  of internal standard (1%  $\text{HNO}_3$ ), resulting in a sample aliquot of 1,000- $\mu\text{l}$  solution and 4 parts per billion (ppb) Indium concentration. Mg, Mn, Sr, and Ba were quantified using a double focusing sector field inductively coupled plasma-mass spectrometer (Finnigan MAT Element 2 ICP-MS). Mg, Mn, Sr, and Ba were selected for analysis because they are the most commonly used elements in studies of Chesapeake Bay biota (e.g., Thorrold et al. 2001). All water samples collected in a given week were analyzed as a batch on the same day. However, samples were randomized within autosampler trays to minimize the effect of instrument drift. Sample solution was introduced using a PFA (perfluoroalkoxy) micro-flow nebulizer (50  $\mu\text{l min}^{-1}$ ) and a PFA spray chamber. Acquisition parameters are summarized in Table 1.

High purity stock standards (High-Purity Standards) were used to prepare multielement calibration standard solutions. Calibration standards were made by diluting the stock standard solution with 1% ultrapure  $\text{HNO}_3$  (by weight) to match typical concentration of Mg, Mn, Sr, and Ba in estuarine waters. The concentration of Indium used as the internal standard in all standard and sample solutions was 4 ppb.

Table 1. Summary of acquisition parameters, concentration of standards (low = L, medium = M, high = H), and mean estimates of precision (% RSD [relative standard deviation]) from ICP-MS analysis of water samples collected in sea grass habitats of Chesapeake Bay from July to September 2001.

Isotopes	<sup>115</sup> In (ppb)	<sup>137</sup> Ba (ppb)	<sup>25</sup> Mg (ppm)	<sup>55</sup> Mn (ppt)	<sup>88</sup> Sr (ppb)	<sup>115</sup> In (ppb)
Resolution	Low	Low	Medium	Medium	Medium	Medium
Mass window	5	5	150	150	150	150
Settling time (ms)	0.0010	0.0010	0.3000	0.0010	0.0010	0.3000
Sampling time (ms)	0.0200	0.0200	0.0200	0.0200	0.0200	0.0200
Samples per peak	200	200	15	15	15	15
Method mass offset	0.0009	0.0002	0.0011	0.0007	-0.0001	0.0007
Standard (L)	4.0100	1.0200	20.0700	50.7900	39.9500	
Standard (M)	4.0100	10.0200	106.0100	250.6900	196.6100	
Standard (H)	4.0200	15.0600	212.4900	503.1800	397.6700	
% RSD		1.1250	3.9000	1.8000	1.8500	

Analytical blank solutions were made up of ultrapure HNO<sub>3</sub> diluted to 1% with milli-Q water. In addition, the sample preparation procedure was monitored by a procedural blank (1% ultrapure HNO<sub>3</sub> and 4 ppb Indium solution), and a quality control check standard (concentration between the two lowest standards) was analyzed sequentially after every six samples.

Calibration curves were established based on known concentrations of the analytes in the calibration standard solutions (categorized as low, medium, and high concentration in Table 1). After acquiring ion intensity data from the mass spectrum, the ion intensity measurement was properly corrected for background interferences based on the analytical blank. Thereafter, the ratio of the analyte ion intensity to Indium ion intensity was plotted against the known concentration of the analyte in the calibration standards (Taylor 2001). Least-square regression was applied to the data with goodness of fit ( $r^2$ ) greater than 0.999 for all analytes. Concentration of each analyte was calculated from the linear equation derived for each calibration curve. After removing the concentration of the procedural blank, the data were further corrected for matrix effects and instrument drift based on the control check standard solution. The precision of measurement (relative standard deviation from repeated measurement of standards, % RSD) achieved for each element is presented in Table 1.

*Statistical analyses*—To test the null hypothesis that there were no significant spatial and temporal differences in the chemistry of surface waters in the lower Chesapeake Bay, we used a month  $\times$  location ( $3 \times 5$ ) factorial multivariate analysis of variance (MANOVA) with response variables Mg, Mn, Sr, and Ba. Based on the experimental design, the sampling unit was a day of sampling in a given fortnight and a given habitat, and these means met the assumption of multivariate normality. Therefore, we performed the MANOVA using the fortnightly mean of each response variable within habitat. A univariate form of the model is presented below:

$$y_{ijk} = \mu + \alpha_i + \beta_j + \alpha\beta_{ij} + \varepsilon_{ijk}$$

where  $\mu$  is the overall mean;  $\alpha_i$  is the effect of the  $i$ th habitat ( $i = 1$  to  $5$ );  $\beta_j$  is the effect of the  $j$ th month ( $j = 1$  to  $3$ );  $\alpha\beta_{ij}$  is the interaction between habitat and month;  $\varepsilon_{ijk}$  is the

sampling error in the  $i$ th habitat, the  $j$ th month, and the  $k$ th fortnight ( $k = 1$  to  $2$ ). Univariate normality for each variable was tested using the Shapiro–Wilk test, whereas homogeneity of variance–covariance matrices was tested using Bartlett’s maximum likelihood ratio test. Multivariate tests of significance were based on Pillai’s trace statistic (Quinn and Keough 2002). Student–Newman–Keuls (SNK) multiple range test was used to determine which habitats differed and which elements contributed to the observed difference (Kuehl 1994).

We used a nonparametric discriminant analysis, the  $k$ -nearest neighbor method ( $k$ -NN), to predict the accuracy of classification of individual water samples to their collection habitat. The  $k$ -NN classifies a new object (water sample) according to its squared distance to a second object. The closest neighbors ( $k$ ) of the new object are found, and the object will be assigned to the habitat that has the majority of its nearest neighbors (Hand 1981; Khattree and Naik 2000; Souza et al. 2003). The constant ( $k$ ) is analogous to a smoothing type parameter. In contrast to fortnight means used in the MANOVA, the statistical distribution of individual variables themselves did not meet the criteria of multivariate normality and homogeneity of variance–covariance matrices. The  $k$ -NN method does not require normality and homogeneity of the variance–covariance matrices (Hand 1981; SAS 1989; Khattree and Naik 2000). We determined classification accuracy from the  $k$ -NN using a Jackknife cross-validation method (Lachenbruch 1975). Using simulations, we determined that  $k = 4$  yielded the smallest total error rate after cross-validation; therefore, results of the  $k$ -NN were based on this value (Hand 1981; Khattree and Naik 2000).

We presented temporal–habitat relationships graphically using nonmetric multidimensional scaling (nMDS) based on Euclidean distance with a convergence criteria of  $S$ -stress  $< 0.05$  (Kruskal and Wish 1978; Schiffman et al. 1981). We used seven variables (Mg, Mn, Sr, Ba, DO, pH, salinity) to build Euclidean distance measures. Because the variables had different absolute magnitudes and ranges, we standardized them to the same scale  $[(x - \mu)/sd]$  prior to computing the distance matrix. Unlike many multivariate graphical methods, the axes in nMDS do not bear a direct relation to ordinations and are not as easily related to the value of the

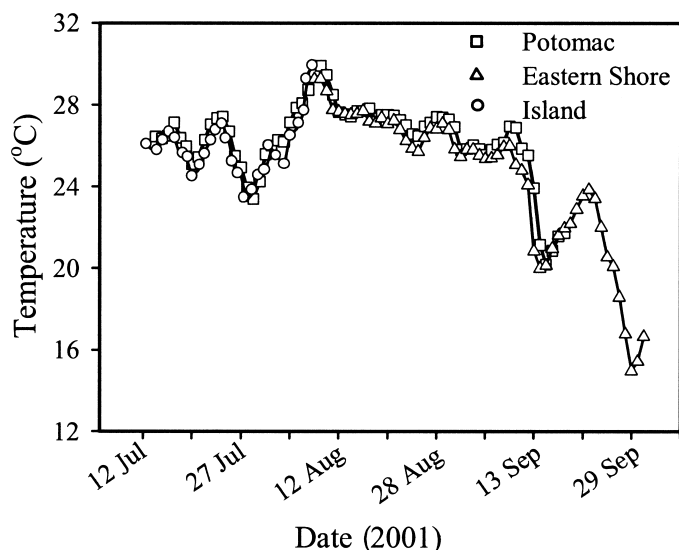


Fig. 2. Mean daily temperature measured in three sea grass habitats from July to September 2001. Note that because of a loss of probes, temperature was not recorded in Island from August to September and in Eastern Shore from July to August. Nevertheless the overall trend showed that there was no difference in temperature between habitats across the bay.

original variables used in developing the two-dimensional projection. However, the value of nMDS is that it preserves relative spatial relations.

In this study all statistical analyses were performed using the SAS statistical software (except for nMDS, which was done in MATLAB) after averaging daily observations in river mouth and excluding all extreme outliers ( $n = 5$ ). Values that were greater or smaller than three times the interquartile range of each variable in a given habitat were defined as extreme outliers.

## Results

*Variation of temperature, salinity, dissolved oxygen, and pH*—Although temperature did change throughout the study, it was the same in all habitats at a given time and changed to the same extent in all habitats over time (Fig. 2). Temperatures averaged 25.7°C in July, 27.4°C in August, and 23.1°C in September. Thus, we can discount the spatial effects of temperature on elemental concentrations.

Salinity differences were significant between habitats with minimal seasonal variation (Fig. 3a). Mean salinity was lower in the upper bay (Island and Potomac) habitats; within habitat variability across months was minimal in Island and York. Thus, the effect of salinity on elemental concentrations (e.g., Ba) in the Island and the York habitats was the most consistent over time. As expected, salinity was higher in the lower bay habitats (Eastern Shore and York).

DO and pH showed slight temporal and spatial variation (Fig. 3b,c). Mean and standard error of DO in surface waters demonstrated an ample supply of oxygen in the water column for all habitats. In fact, the water column in these shallow waters was well mixed during the sampling period. pH

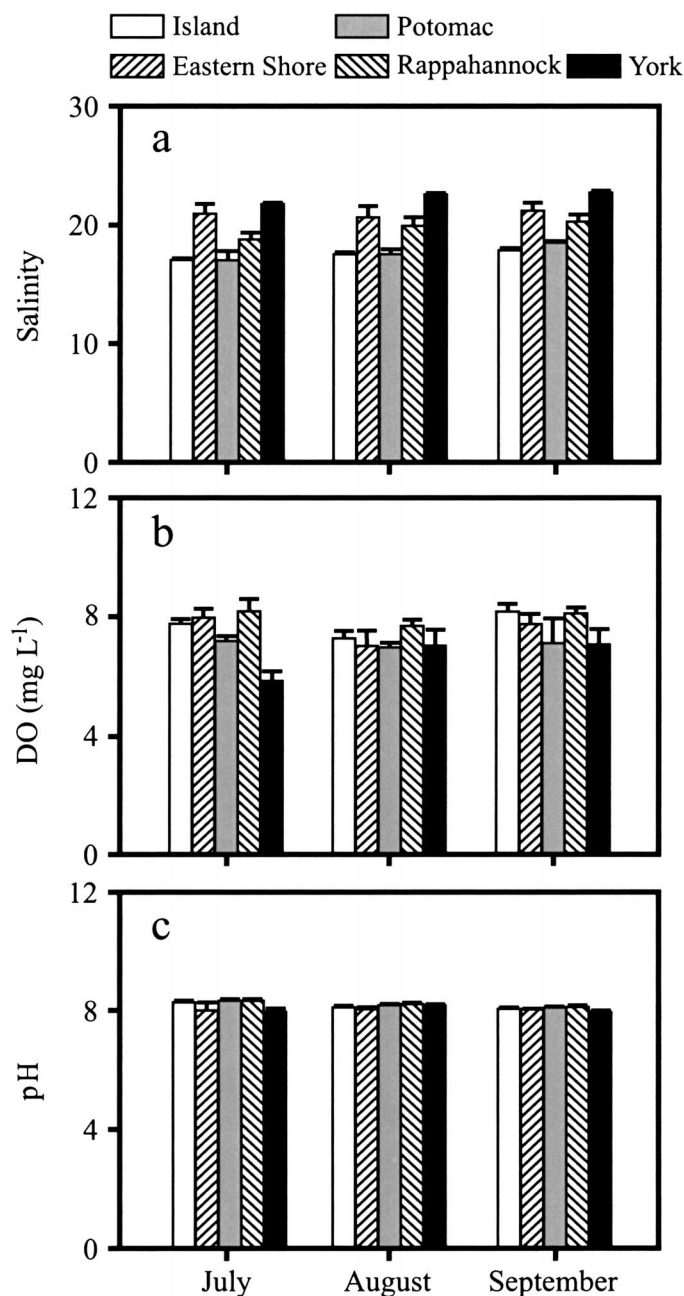


Fig. 3. Spatial and temporal variation in (a) salinity, (b) dissolved oxygen (DO), and (c) pH measured in surface water of sea grass habitats of Chesapeake Bay from July to September 2001.

was alkaline and typical of seawater with an overall mean of 8.11.

*Mixing patterns and variability of Mg, Mn, Sr, and Ba*—Figure 4 shows the variation of Mg, Mn, Sr, and Ba along the salinity gradient. As anticipated Mg, Sr, and Ba exhibited conservative behavior with increasing salinity across months. The elemental compositions in samples from the northern habitats, Island and Potomac, were distinctly different from the southern habitats, Rappahannock, York, and Eastern Shore (Fig. 4). Mg concentrations in samples from

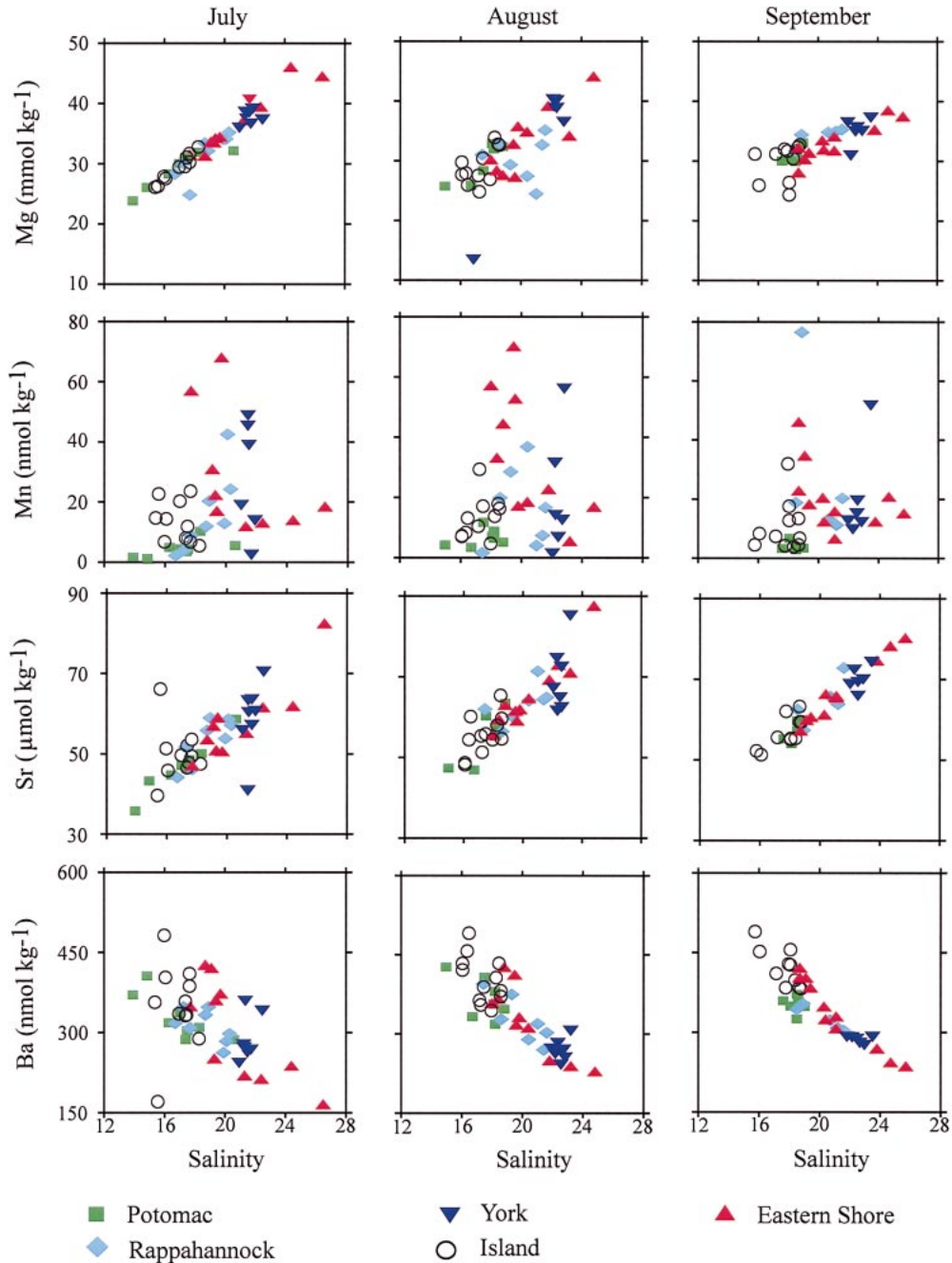


Fig. 4. Variation of Mg, Mn, Sr, Ba, and salinity of sea grass habitat surface waters in Chesapeake Bay in 2001.

Table 2. Two-way MANOVA results for Mg, Mn, Sr, and Ba measured in surface waters of sea grass habitats of Chesapeake Bay from July to September 2001. All tests were based on the Pillai's trace statistic.

Source	Value	<i>F</i>	Numer- ator df	Denom- inator df	<i>p</i>
Habitat	1.95	3.58	16	60	0.0002
Month	0.95	2.96	8	26	0.017
Habitat × month	1.48	1.1	32	60	0.3621

the northern and southern habitats showed similar spatial distribution patterns to that of Sr along the salinity gradient (Fig. 4). In contrast to Mg and Ba, Mn exhibited nonconservative behavior along the salinity gradient (Fig. 4).

*Analysis of variance*—We present the results of the two-way MANOVA (Table 2) based on the fortnightly means of Mg, Mn, Sr, and Ba within habitats. The fortnightly means of each variable were normally distributed within habitat and within month; therefore, we assumed multivariate normality error (Quinn and Keough 2002). Further, based on the like-

Table 3. Two-way ANOVA test results for Mg, Mn, Sr, and Ba measured in surface waters of sea grass habitats of Chesapeake Bay from July to September 2001.

Dissolved element	df	MS	F	p
<b>Mg</b>				
Habitat	4	61.39	47.12	0.0001
Month	2	0.57	0.44	0.6539
Habitat × month	8	5.84	4.48	0.0061
<b>Mn</b>				
Habitat	4	343.57	12.76	0.0001
Month	2	27.82	1.03	0.3799
Habitat × month	8	12.57	0.47	0.8609
<b>Sr</b>				
Habitat	4	190.93	12.58	0.0001
Month	2	267.51	17.63	0.0001
Habitat × month	8	2.51	0.17	0.9926
<b>Ba</b>				
Habitat	4	11,047.70	16.89	0.0001
Month	2	105.17	1.62	0.2314
Habitat × month	8	298.39	0.45	0.8681

likelihood ratio test, we found that the variance–covariance matrices were homogeneous among habitats ( $\chi^2 = 25.879$ ,  $df = 20$ ,  $p = 0.1698$ ) and among months ( $\chi^2 = 49.794$ ,  $df = 40$ ,  $p = 0.1379$ ). Thus, we conclude that for these four elements MANOVA could be validly used to test for distinct differences in elemental composition between habitats.

The MANOVA results showed no significant interaction between month and habitat (Table 2). These results suggested that the spatial difference in the dissolved element chemistry of sea grass habitats were independent of time. Therefore, though the concentration of these elements varied temporally in the bay, the chemical and physical processes that regulated their spatial distribution remained the same.

Once differences among habitats had been identified, we performed pairwise comparison of habitats based on the SNK multiple range test on each of these variables (Mg, Mn, Sr, and Ba) to isolate which habitats were different (Tables 3 and 4). The SNK tests confirmed the uniqueness of the Island habitat, since it differed significantly from all habitats in Ba, from all habitats but Rappahannock in Mn, and from all habitats but Potomac in Sr. Potomac was significantly

different from all habitats in Mn and had the lowest mean Mn concentration. As expected, the York habitat had the lowest mean Ba concentration and was significantly different from all habitats, but was similar to Eastern Shore in Sr, and to Eastern Shore and Rappahannock in Mn.

The SNK results for Mg, however, differed from the other elements by exhibiting a significant interaction between month and habitat. The interaction reveals that Mg concentration was significantly different between months in the southern habitats (Rappahannock, York, and Eastern shore) but similar across months in the northern habitats (Potomac and Island). The month of September was significantly different from July and August in York and Rappahannock, whereas the month of July was significantly different from August and September in Eastern Shore. These results cannot be explained solely by temperature or salinity but may be a product of their interaction. The Mg results illustrated the importance of using MANOVA. Because MANOVA combined all four variables (Mg, Mn, Sr, Ba) to derive a composite signature (Quinn and Keough 2002), it is possible to identify and quantify differences between sea grass habitats that are unresolvable by univariate analysis. Indeed, the MANOVA procedure provided a better test for interaction, showing that in multivariate statistical space differences in habitat and month are independent.

*Discriminant analysis*—Having established differences among habitats independently of month using MANOVA, we further quantified these differences using the  $k$ -NN discriminant function analysis. The  $k$ -NN results in Table 5 show that Island and York had the highest accuracy of classification, followed by Potomac and Eastern Shore. Samples in Rappahannock were very poorly classified, but this is consistent with the results of the SNK test, which showed that the dissolved element chemistry of this habitat was not significantly different from the other habitats. Classification rates in Potomac and Eastern Shore were moderate but satisfactory when considering that because of random chance alone, there is only a 20% probability that samples would be classified correctly to their collection habitat. Classification rates were obtained after cross-validation, and thus they are unbiased estimates. High accuracy in allocating samples to the York habitat is a result of mixing between oceanic and fluvial waters. Compared with the other habitats, York

Table 4. SNK multiple range pairwise test results for Mn, Sr, and Ba measured in surface waters of sea grass habitats of Chesapeake Bay from July to September 2001. Mg results not provided because of the significant interaction. Letters do not indicate a specific habitat, rather they show habitats that are similar for a given element. Habitats that are similar share the same letter distinguishing them from habitats that are different. For example, the letter A shows that Eastern Shore has the same level of concentration in Mn as York and Rappahannock.  $n = 6$  in all cases.

Habitat	Mn		Sr		Ba	
	SNK group	Mean	SNK group	Mean	SNK group	Mean
York	A	23.16	A	66.23	C	280.18
Eastern Shore	A	22.59	A, B	62.83	B	320.47
Rappahannock	A, B	15.81	B	60.12	B	320.57
Island	B	12.12	C	54.00	A	396.6
Potomac	C	5.06	C	53.13	B	347.81



Table 5. Results of nonparametric discriminant function analysis using  $k$ -nearest neighbor method ( $k$ -NN,  $k = 4$ ) where water samples were classified to the original collection habitats based on the concentration of Mg, Mn, Sr, and Ba. Percentages of classification of water samples were obtained after Jackknife cross-validation. Bold indicates classification rate for each habitat.

Sample source	Cross-validation accuracy (%)				
	Island	Eastern Shore	Potomac	Rappahannock	York
Island ( $n = 32$ )	<b>81.3</b>	3.1	15.6	0.0	0.0
Eastern Shore ( $n = 30$ )	10.0	<b>60.0</b>	3.3	6.7	20.0
Potomac ( $n = 21$ )	23.8	0.0	<b>71.4</b>	4.8	0.0
Rappahannock ( $n = 19$ )	5.3	31.6	15.8	<b>36.8</b>	10.5
York ( $n = 17$ )	0.0	11.8	0.0	5.9	<b>82.4</b>

is chemically most similar to Eastern Shore, which is an oceanic end member but differs from the latter by the greater influence of freshwater. Strikingly, we could predict with high accuracy samples collected in the Island habitat. As discussed above, the clear separation of Island from the Eastern and the Western Shore habitats may not be due simply to mixing processes alone, but rather to the interaction of mixing and other physical and chemical processes.

*Nonmetric multidimensional scaling analysis*—The separation between the habitats across months is shown graphically in Fig. 5. The separation of habitats along dimension 1 follows the salinity gradient, and therefore it distinguishes higher Sr concentrations as more negative and higher Ba concentrations as more positive. The upper bay habitats (Potomac, Rappahannock, and Island) have values of  $-0.5$  to  $+2.0$ , while the lower bay habitats (York and Eastern Shore) have values from  $-3$  to  $-0.75$ . The separation of habitats along dimension 2 is more complex. There is no clear relation that separates habitats or months along this axis. Note that upper bay habitats (Potomac, Rappahannock, and Island) show a general pattern of September > August > July along dimension 2 from positive to negative values, while lower bay habitats (York and Eastern Shore) show a gener-

ally opposite pattern. This axis displays, in part, the interaction between month and habitat in Mg concentrations that were evident in the univariate analyses in Table 3. Nonetheless, habitats are fully resolvable graphically and support the parametric results that we obtained. Thus by weight of evidence, using parametric, nonparametric, and graphical techniques we show that habitat chemistry is unique and spatially separable.

## Discussion

The dissolved Mg, Mn, Sr, and Ba chemistry of sea grass habitats along and across the lower Chesapeake Bay is significantly different, and the variation in chemistry cannot be solely attributed to salinity. Other factors such as redox cycling of Mn may also contribute to these differences. Because the chemistry of the dissolved load in the Island habitat is distinct from that of Western and Eastern Shore habitats, spatial variations are fully resolvable across all sea grass habitats in the lower bay.

The dissolved elemental chemistry of sea grass habitats in the lower Chesapeake Bay is spatially different along and across the estuary. As in any wide estuary, we anticipated variation between southern and northern habitats as well as between the Eastern and Western Shores. It is well known that during estuarine circulation, progressive mixing of freshwater and oceanic water leads to depletion of elements in the dissolved load along the salinity gradient (e.g., Guieu et al. 1998; Zwolsman and van Eck 1999). Austin (2004) reported that mean salinity measured along the main stem of the bay over several years, between our sampling areas, shows a gentle but uniform gradient. Our results demonstrate that this gradient is preserved in shallower habitats and plays a significant role on the elemental composition of surface waters. The temporal maintenance of the differences in salinity and elemental composition between habitats may be related to the fact that both mean salinity and salinity stratification are strong functions of freshwater inputs in the bay. Mean salinity and salinity stratification respond to variability in fluvial inputs on a scale of approximately 90 days (Austin 2004), which corresponds to the temporal scale of our study. Further, in a wide system such as Chesapeake Bay, Coriolis acceleration may modify typical estuarine circulation restricting outflow of freshwater (e.g., from the Susquehanna, Potomac, Rappahannock, York, and James Rivers) toward the Western Shore and inflow of oceanic water toward the

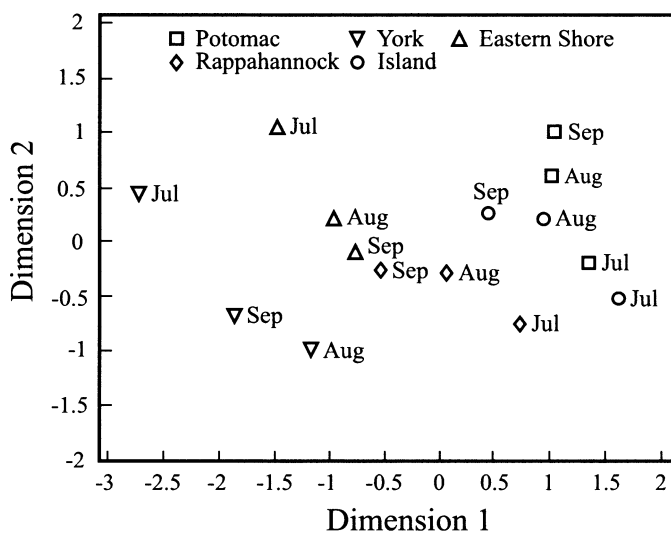


Fig. 5. Plot of temporal-habitat relationships based on nonmetric multidimensional scaling using Euclidean distances of salinity, DO, pH, Mg, Mn, Sr, and Ba.

Eastern Shore (Pritchard 1952; Austin 2004). This may result in a lateral density gradient and consequently, as demonstrated in this study, in a heterogeneous distribution of dissolved elements from the Western to the Eastern Shore. However, the lateral density gradient alone cannot explain the difference between the chemistry of sea grass habitats. For the elements under investigation, beside salinity, competing complexation reactions and redox cycles may interact to produce the level of spatial variability observed both along and across the estuary, including the uniqueness of the Island habitat.

The spatial distribution and concentration of Mg and Ba are consistent with conservative behavior of these elements in estuaries, but they also exhibit subtle differences resulting from competing physical and chemical processes occurring in sea grass habitats. Mg concentration levels observed in these habitats may be a result of the interaction of both temperature and salinity, with temperature having perhaps a lesser role in the two most northern habitats, Potomac and Island, which are strongly influenced by freshwater inputs. In Chesapeake Bay, dissolved Ba concentrations typically reach a maximum (300–400 nmol kg<sup>-1</sup>) between a salinity of 5 and 10 (Coffey et al. 1997). These concentration maxima derive from the release of Ba from riverine particulate matter by exchange reactions with Mg<sup>+2</sup> and Ca<sup>+2</sup> in oceanic waters (Hanor and Chan 1977; Hilmar and Kogut 1999). In this study we found similar levels of dissolved Ba in both the Island and Potomac habitats. These two habitats are located in the lower bay. Their Ba concentrations may be simply the result of physical mixing of fluvial and oceanic particulates (Zwolsman and van Eck 1999). However, they may also correspond to desorption of Ba from river sediments deposited in periods of high river discharge to sea grass habitats either by storm events or high winter river discharge. Under such conditions, sediment accumulated in sea grass habitats would slowly release Ba<sup>+2</sup> in the summer by exchange with seawater ions, such as Mg<sup>+2</sup>, when salinity increases and freshwater discharges are low. These mechanisms were previously identified by Carroll et al. (1993) in sediment deposited in mangrove habitats and on islands of the Ganges–Brahmaputra mixing zone in the bay of Bengal. Coffey et al. (1997) noted that such large releases of Ba within an estuary are characteristic of the Chesapeake Bay. These authors argued that salt marshes of the bay behave as storage sites in periods of high supply of particulate Ba. The uniqueness of the chemistry of the Island habitat may be a direct effect of these processes. The Island habitat is located mid-bay in the transition zone between the shallow and the deeper topography, where the Susquehanna River accounts for 87% of the freshwater input (Pritchard 1952; Sholkovitz and Elderfield 1988). River discharges from the Susquehanna usually peak in the spring, corresponding to snow melt within the watershed. Thus the geographical location of the Island habitat makes it a suitable sink for winter sediments of the Susquehanna River. The dynamics of surface water chemistry of the Island habitat may reflect the greater influence of river flow and sediment loading of the Susquehanna River.

In contrast to the divalent cations Mg, Sr, and Ba, Mn is a redox-sensitive element whose concentration varies sea-

sonally in Chesapeake Bay, reaching a maximum in summer. Mn concentrations of sea grass habitats reflected the reduction of Mn<sup>+4</sup> in surface sediments and bottom waters and subsequent transport of Mn<sup>+2</sup> into surface waters and shallow sea grass habitats of the bay (Eaton 1979; Gavis and Grant 1986; Sholkovitz et al. 1992). The reduction of Mn<sup>+4</sup> and transfer of Mn<sup>+2</sup> occurs in the bay when suboxic and anoxic conditions develop in spring and summer (Taft et al. 1980; Seliger et al. 1985). Eaton (1979) demonstrated that remobilization of Mn from reducing sediments controlled most of the supply of Mn into surface waters of the bay. Gavis and Grant (1986) suggested this supply of Mn<sup>+2</sup> also originated from the reduction and dissolution of oxidized manganese particles formed in deep anoxic water of the bay. In this study, the magnitude of these processes varies at very fine spatial scale, leading to nonconservative behavior of Mn and a significant difference in its concentration in sea grass habitats that are separated by 9 to 50 km both along and across the estuary.

The discrimination of sea grass habitats based on their chemistry has important ecological implications. First, the small-scale spatial differences in the chemistry of sea grass surface waters suggest that organisms living in these habitats are experiencing different water masses. Individual populations and species will respond differently to such small-scale environmental changes depending on their evolutionary experience (Livingston 1984) and their degree of tolerance of salinity and elemental composition of surface waters. Distribution of sea grass habitats and their resident species are mostly associated with large-scale changes in salinity and seasonal temperature in the bay. Moore et al. (2000) found that high salinity communities in the bay were dominated by the sea grass *Zostera maritima* in winter, spring, and summer, whereas in the lower salinity communities *Ruppia maritima* was the most prevalent species in the fall. Similarly, Orth and Heck (1980) associated abundance and diversity of fish and decapods in these habitats to seasonal change in temperature. However, at the smaller scale it is not fully understood why this submerged aquatic vegetation (SAV) occurs in one area but is absent just a few meters away. Koch (2001) argued that beyond light, geochemical parameters can play an important role in controlling small-scale distribution of SAV. He pointed out that substances such as hydrogen sulfide and reduced manganese, among others, can be potentially toxic to estuarine and marine vegetation. Thus, aside from salinity, the distribution of manganese observed in our study may significantly affect the distribution and composition of SAV in the bay at small scales that were previously unnoticed.

Second, spatial differences in the chemistry between sea grass habitats also reflect variation in habitat and water quality. Thus, differential water masses may cause differential growth rates of resident organisms, affecting their survivorship and fitness. Many species use the sea grasses as nurseries; thus, the growth of their larvae and juveniles is likely to be habitat specific. Likewise, the community structure of these habitats and thus their relative ecological importance may differ at small scales.

In conclusion, using both parametric and nonparametric statistical methods we showed significant spatial difference

in the chemistry of surface waters longitudinally and laterally in the lower Chesapeake Bay. Despite temporal variability, sea grass habitats were distinct not only because of the influence of salinity but also due to competing chemical reactions and redox control of Mn. The chemistry of the York habitat was distinct, but this was mostly due to the effects of physical mixing of fresh and ocean waters. The chemistry of the Island habitat was unique, potentially because of the influence of Coriolis acceleration and river discharges from the Susquehanna River. Finally, our results suggest that biota that used these sea grass habitats for seasonal nurseries experience different water masses and different chemistries.

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