

Coupling of near-bottom seston and surface sediment composition: Changes with nutrient enrichment and implications for estuarine food supply and biogeochemical processing

R. H. Carmichael¹ and I. Valiela

Boston University Marine Program, Marine Biological Laboratory, Woods Hole, Massachusetts 02543

Abstract

We compared near-bottom seston and surface sediment composition in Cape Cod estuaries receiving different N loads to determine whether eutrophic-driven changes in seston and sediment composition occur in tandem and what implications such coupling has for the quantity and quality of particles available as food for benthic consumers. $\delta^{15}\text{N}$ signatures in seston and sediment increased with increasing N loads to estuaries and linked particles in nearshore seston and sediment to land-derived wastewater sources. $\delta^{13}\text{C}$ signatures in seston and sediment reflected C inputs primarily from microalgae. Sediments, however, were consistently lighter in $\delta^{15}\text{N}$ and heavier in $\delta^{13}\text{C}$ compared with seston among our estuaries and in other estuaries worldwide, which suggests a seston–sediment biogeochemical coupling that may be independent of estuary-specific differences. In Cape Cod estuaries, N enrichment increased microalgal production in seston and sediment in nearshore areas, and higher N loads decreased C:N in sediments, but not in seston. The biogeochemical coupling reflected in isotopic signatures in seston and sediment persisted despite these changes associated with N enrichment and differences in grazer abundance, salinity, and flushing times across estuaries. Differences in isotopic signatures in benthic algae compared with phytoplankton were consistent with isotopic differences in sediment compared with seston, and microalgal production was the only aspect of composition that responded similarly to N loading in both seston and sediment across estuaries. The consistent coupling between seston and sediment composition, therefore, was likely related to differences in microalgal composition and, in turn, the type and quantity of particles available as food to consumers at the sediment–water interface.

In shallow estuaries subject to mixing, composition of near-bottom suspended particulate matter (seston) may be influenced by particles resuspended from surface sediments (Baillie and Welsh 1980; Lukatelich and McComb 1986; Lucas et al. 2000). This potential link between seston and sediment composition in near-bottom waters is of interest to understand a variety of estuarine features, including food quantity and quality available to primary consumers (Fegley et al. 1992; Riera 1998; Carmichael et al. 2004a) and the effects of biogeochemical processes such as inorganic nutrient exchange at the sediment–water interface and decomposition of organic matter (Sundbäck et al. 1991; Zimmerman and Canuel 2001; Tobias et al. 2003). Despite the likely importance of interactions between near-bottom seston and surface sediment, few studies have set out to assess the potential for coupling between seston and sediment in terms of similarity in composition or whether seston and sediment composition changes in tandem in response to environmental variation.

¹ Current address: University of Maine at Machias, Machias, Maine 04654 (rcarmichael@maine.edu).

Acknowledgments

This work was supported by grants from the Woods Hole Oceanographic Institution Sea Grant—National Oceanic and Atmospheric Association National Sea Grant College Program (NA86RG0075, project R/M-51-PD), the Palmer–McLeod Fellowship Program at Boston University to R.H.C., and the Humes Alumni Award at the Boston University Marine Program to R.H.C. We thank Anne Giblin, Paul Barber, and Lauren Mullineaux for comments on this manuscript. We also thank Andrea Shriver, Rachel Allen, and Erica Weiss for assistance with field and lab work, the U.C. Davis stable isotope facility for analyzing samples, and the Waquoit Bay National Estuarine Research Reserve and the towns of Mashpee, Falmouth, and Wareham, Massachusetts, for facilitating access to study sites.

Increased nutrient enrichment and resulting eutrophication potentially alter abundance and composition of particles at the sediment–water interface (Cloern 2001; Kang et al. 2003). Eutrophication is associated with increased primary production (Granéli and Sundbäck 1985; Cloern 2001), accumulation of detritus, and microbial activity in seston and sediment (Köster et al. 1997; Zimmerman and Canuel 2001). Eutrophic-driven changes in near-bottom seston and surface sediment may, in turn, affect growth and composition of benthic consumers (Fegley et al. 1992; Carmichael et al. 2004b). By evaluating changes in seston and sediment composition across estuaries receiving different N loads, we can test the similarity of seston and sediment composition as N loads increase, defining the extent and nature of potential coupling between seston and sediment. We can then relate eutrophic-driven changes in near-bottom seston and surface sediment composition to the availability of food sources at the base of benthic food webs.

Coupling of near-bottom seston and surface sediment composition can be defined by use of stable isotopes along with evaluating organic composition and external controls of seston and sediment attributes. First, responses of seston and sediment can be linked to estuary-specific N loads and traced up food webs using N and C isotopes (Peterson and Fry 1987; Michener and Schell 1994). N isotopic ratios increase with increasing wastewater inputs to coastal estuaries (McClelland and Valiela 1998a; Mayer et al. 2002), while land-derived C sources typically have lighter C isotopic signatures than marine sources (Peterson and Fry 1987; Currin et al. 1995; Cloern et al. 2002). These differences in isotopic composition of seston and sediment can be traced through the food web since isotopes are fractionated with each trophic step (Peterson and Fry 1987). Second, changes in abun-

dance and nutritional value of particles in seston and sediment can be quantified by measuring chlorophyll *a* (Chl *a*) concentration and C and N composition (Fegley et al. 1992; Valiela 1995). Third, changes in seston and sediment composition across different locations may be affected by external controls including estuary flushing times, salinity, temperature, abundance of grazers, and sediment grain size (Cloern 2001; Thornton et al. 2002), making these estuary-specific variables potentially important to assessing seston–sediment coupling.

Estuaries of Cape Cod provide favorable locations to study the effects of different N loads on coupling of near-bottom seston and sediment composition. Different land uses on the watersheds of Cape Cod estuaries have resulted in different land-derived N inputs to receiving estuaries (Costa et al. unpubl.; Kroeger et al. 1999; Valiela et al. 2000). These N loads are large enough to span most of the range of land-derived N loads common to coastal estuaries (Valiela et al. 1992, 2000). We can thus compare near-bottom seston and surface sediment composition across these estuaries to determine whether different N loads alter seston–sediment coupling.

In this paper, we define similarities and differences in the composition of near-bottom seston and surface sediment to discern the extent of coupling between seston and sediment composition, compare changes in seston and sediment composition across estuaries receiving different land-derived N loads, and discern implications of these relationships for estuarine food supply. To do this, we measured $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ values, Chl *a*, carbon (C), and nitrogen (N) concentrations in near-bottom seston and surface sediment in each estuary. We then compared our results with similar data collected in other estuaries distributed worldwide to see whether the Cape Cod results were generally applicable. We also measured temperature, salinity, sediment grain size, and number of grazers to determine how external controls may have affected the coupling of seston and sediment composition at our sampling sites.

Methods

Sampling procedure—To define seston and sediment composition and compare changes in composition as N enrichment increases, we collected near-bottom seston and surface sediment samples in eight Cape Cod estuaries, representing a wide range of N loads (Fig. 1, Table 1). Determination of N-loading rates is described in detail elsewhere (Valiela et al. 1997, 2000) but included measuring and/or modeling N inputs based on data collected for the entire watershed and N concentrations in groundwater collected at the seepage face around the periphery of each estuary. In this study, we collected two samples of seston and sediment at each of two sites per estuary, every 2 weeks from early June to mid-September 2001, for a total of 224 samples each of seston and sediment. The two sampling sites in each estuary were chosen to have similar depth (~ 1 m at mean low water), flow regimes, temperatures, and sediment grain size (Table 1). We sampled across equivalent low and intermediate tides in each estuary to capture similar tidal variation. To collect seston and sediment samples relevant to assessing benthic food webs, we further selected sites near shore but subtidal,

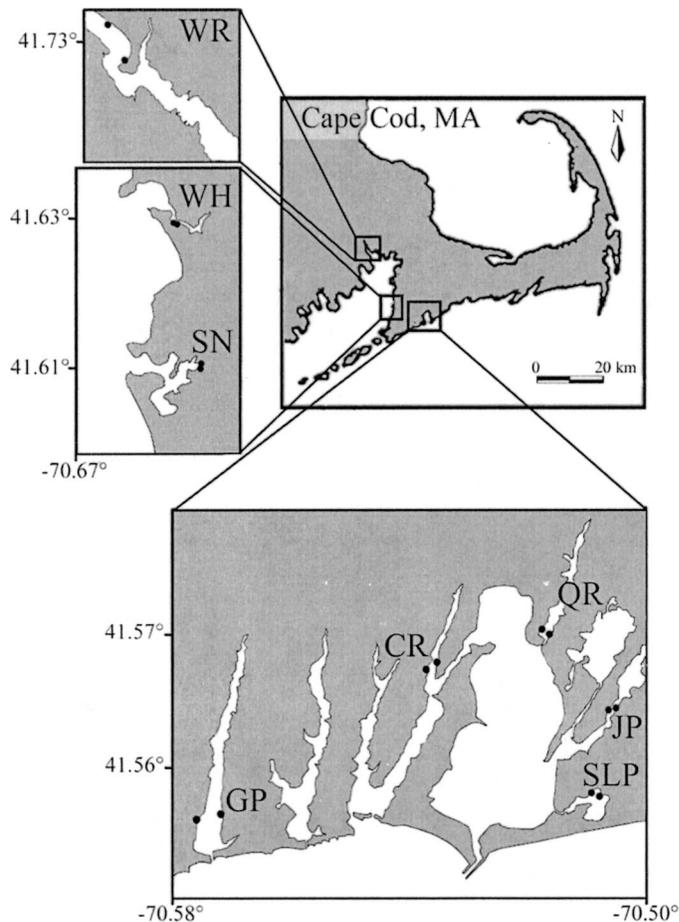


Fig. 1. Sampling sites in eight estuaries of Cape Cod, Massachusetts. WR = Weweantic River, WH = Wild Harbor, SN = Snug Harbor, GP = Green Pond, CR = Childs River, QR = Quashnet River, JP = Jehu Pond, SLP = Sage Lot Pond. Black dots indicate sampling sites in each estuary.

where primary consumers were abundant (Carmichael et al. 2004b).

To collect near-bottom seston, we sampled water ~ 10 cm from the sediment surface using a Wildco horizontal water sampler. We chose the Wildco sampler because preliminary studies determined that it efficiently captured near-bottom water samples without capturing sediments artificially resuspended by the sampling process. To avoid and detect sediment disturbance during sampling, we measured water depth carefully before collecting samples, changed sampling locations if disturbance was suspected, and collected a sufficient number of samples to allow statistical determination of any anomalous data points. Two liters of each water sample (200 μm prefiltered) was then filtered onto a preashed 0.7- μm Whatman GF/F filter.

To collect sediment samples, we used a 1-cm diameter syringe corer to take the top 3 cm of sediment and pooled sediment from three replicate cores at each sampling site. Sampling sediment to a depth of 3 cm was likely to capture not only the majority of active Chl *a* in Cape Cod sediments (Lukatelich and McComb 1986; Cahoon et al. 1999), but also the portion of sediment that is most likely important to

Table 1. N load, estuary flushing time (T_r), mean water temperature, salinity, density of snails (*N. obsoletus*), and sediment and seston characteristics at two sampling sites in eight Cape Cod estuaries (cf. Fig. 1).*

Estuary	N load (kg N ha ⁻¹ yr ⁻¹)	T_r (d)	Site	Temp (°C)	Salinity	Snails (No. m ⁻²)	Sediment		Seston	
							Silt and clay (%)	Sand (%)	SPM (mg L ⁻¹)	POM (mg L ⁻¹)
Sage Lot Pond	14	1.50†	1	25.3	29.8	0	2	97	17.0±6.0	3.9±1.0
			2	25.1	25.4	0	9	91	21.5±6.5	6.1±1.3
Jehu Pond	21	1.10‡	1	24.9	29.4	0	4	96	27.4±3.9	5.5±0.7
			2	25.0	28.8	0	6	94	25.2±5.7	5.0±0.7
Wild Harbor	65	1.80§	1	24.4	24.9	0	1	88	28.9±3.5	5.8±1.1
			2	24.6	23.9	0	1	83	36.5±4.3	7.6±1.4
Green Pond	178	1.40	1	24.5	25.5	360	11	86	42.6±7.6	8.6±1.6
			2	25.1	29.0	333	8	84	23.0±3.7	5.5±0.7
Snug Harbor	236	1.80‡	1	25.4	18.4	0	8	78	27.2±4.9	6.9±1.8
			2	23.8	25.0	0	14	81	59.1±12.5	9.0±1.9
Weweantic River	339	1.14§	1	23.9	18.3	333	3	94	34.8±6.7	8.1±1.5
			2	24.0	17.7	158	3	97	32.3±7.9	7.3±1.0
Quashnet River	353	1.70†	1	23.9	21.9	0	1	97	18.6±4.9	5.8±0.8
			2	23.1	23.1	0	4	96	14.2±1.6	5.3±0.5
Childs River	601	2.00†‡	1	23.2	22.9	104	14	86	28.0±5.6	6.6±0.7
			2	25.0	21.1	52	9	91	26.4±3.5	6.2±0.5

* Sediment characteristics include percentage by weight of silt and clay (<63 μ m) and sand (63 μ m to 2 mm). Seston data include total (SPM) and organic (POM) suspended particulate matter. N loading rates are from Valiela et al. (1997, 2000), except Wild Harbor and Weweantic River for which values were modified from Costa et al. (unpubl. data) according to Valiela et al. (2002).

† J. Kremer (unpubl. data).

‡ Kroeger et al. (in press).

§ Costa (unpubl. data).

|| Hoves and Ramsey (unpubl. data).

estuarine food supply (Carmichael et al. 2004a,b). We measured salinity and water temperature ~10 cm from the sediment surface at each site when seston and sediment samples were collected. Salinity and temperature were measured using a YSI 95 digital meter.

Stable isotope analysis—To determine isotopic signatures of seston and sediment, seston filters and subsamples of sediment from each site were dried to a constant weight at 60°C, and sediments were ground to a powder. C and N in both sample types were analyzed by continuous flow isotope ratio mass spectrometry (20–20 mass spectrometer, PDZ Europa) after sample combustion to CO₂ and N₂ in an online elemental analyzer (PDZ Europa Automatic Nitrogen and Carbon Analyzer-Gas Solid Liquid). Gases were separated on a Carbosieve G column (Supelco) before introduction to the isotope ratio mass spectrometer (IRMS).

Organic composition of seston and sediment—To determine the quantity and quality of organic particles recovered from seston and in sediment, we measured Chl *a*, C, and N concentrations, and C:N in both seston and sediment as well as the concentration of total suspended particulate matter (SPM) and particulate organic matter (POM) in seston. To measure Chl *a* concentration in seston and sediment, we extracted bulk sediments and filters containing seston with 90% acetone and used the spectrophotometric methods and equations of Lorenzen (1967). To determine C and N concentrations, we combusted filters and sediment in a Perkin-Elmer 2400 CHN elemental analyzer. We acidified sediments overnight (~12 h) by fuming with concentrated HCl to re-

move carbonates before combustion. This relatively mild method of acidification did not alter organic nitrogen concentrations. To determine total and organic particulate matter in seston, we quantified weight of seston per volume of water filtered and ashed filters at 490°C for 4 h.

Grazer abundance—To determine the potential effects of grazers on microalgae biomass, we noted the presence of any grazers at each site during the study. Snails were the only grazers consistently found at numbers higher than 10 per site where they were found. We quantified the potential effect of snails on algal biomass by counting the number of snails in four randomly oriented 30-cm² plots, one time at each site, during the final 2 d of sampling. Results of this counting were consistent with general patterns in snail abundance observed throughout the study.

Sediment grain size—To determine sediment grain size, we sieved subsamples of wet sediment from each site. We sorted sediments into three fractions: clay + silt (<63 μ m), sand (63 μ m to 2 mm), and gravel (>2 mm) (Wentworth 1922). Each particle size fraction was dried and weighed to determine percentage composition.

Statistics—For regression analyses N-loading rates and percentage wastewater were considered to have no error, allowing use of type I regression. Type II regression analysis was used for comparison with all other independent variables. For most comparisons, data were combined to calculate a mean value for each of the eight Cape Cod estuaries, with each data point representing ~28 individual samples.

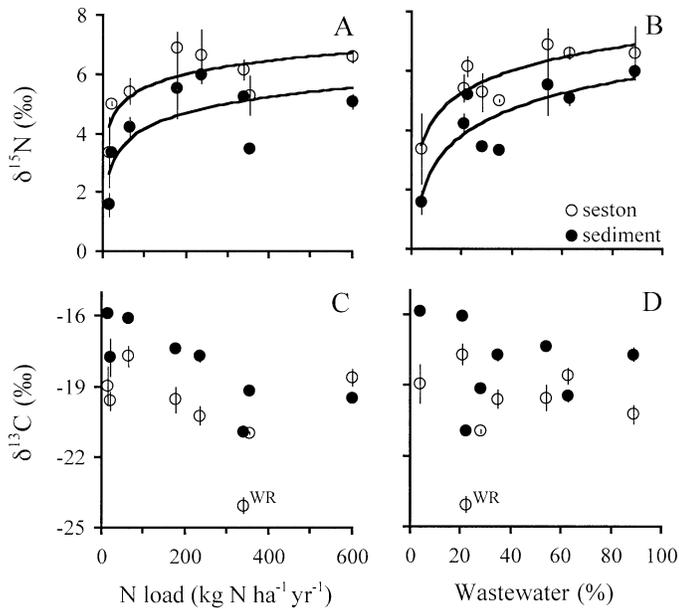


Fig. 2. (A and B) Mean (\pm standard error) $\delta^{15}\text{N}$ and (C and D) $\delta^{13}\text{C}$ in seston and sediment compared with (A and C) N-loading rate and (B and D) percentage contribution of wastewater to total N load among eight Cape Cod estuaries. N-loading rates are shown in Table 1, and percentage wastewater contributions are from Costa (unpubl. data), modified according to Valiela et al. (2002), Kroeger et al. (1999), and Valiela et al. (2000). ($\delta^{15}\text{N}$ vs. N load, seston, $y = 0.66 \ln x + 2.48$, $r^2 = 0.63$, $F_7 = 10.24$, $p = 0.02$; sediment, $y = 0.78 \ln x + 0.56$, $r^2 = 0.55$, $F_7 = 7.34$, $p = 0.04$; $\delta^{15}\text{N}$ vs. percentage wastewater, seston, $y = 1.09 \ln x + 2.00$, $r^2 = 0.80$, $F_7 = 24.36$, $p = 0.003$; sediment, $y = 1.30 \ln x + 0.07$, $r^2 = 0.72$, $F_7 = 15.76$, $p = 0.01$). WR = Weweantic River. Where no error bars are present, error was smaller than symbol.

Statistical tests were performed as indicated in the text using StatView 5.0.1.

Results and discussion

$\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ in seston and sediment—N isotopic signatures in near-bottom seston and surface sediment showed significant logarithmic increases with increasing N load to the watersheds of the eight Cape Cod estuaries (Fig. 2A) and with increasing contribution of wastewater to total N load (Fig. 2B). Wastewater contribution to N load was a better predictor of $\delta^{15}\text{N}$ signatures in seston and sediment ($r^2 = 0.80$ and 0.72 , respectively) than N-loading rate ($r^2 = 0.63$ and 0.55 , respectively), consistent with McClelland and Valiela (1998a) and Cole et al. (2004). The magnitude of $\delta^{15}\text{N}$ values and the logarithmic responses we measured have been found in other estuaries and freshwater bodies (Lake et al. 2001; Cole et al. 2004; Carmichael et al. 2004a). These data emphasize potential for N enrichment to affect detectable changes in characteristics of near-bottom water and surface sediment particularly at relatively low N loads (Carmichael et al. 2004a).

The precise reason for a logarithmic response by $\delta^{15}\text{N}$ in seston and sediment to increasing N loads is unknown, but it may be related to changes in abundance and composition

of primary producers across estuaries. Previous studies have found the magnitude of $\delta^{15}\text{N}$ in producers varies among species, and producer species composition and dominance may change with increasing N loads to estuaries (Valiela et al. 1992; McClelland and Valiela 1998a,b; Carmichael et al. 2004b). If these changes occur as N loads increase but at relatively low N loads (Carmichael et al. 2004a,b), $\delta^{15}\text{N}$ values in seston and sediment across estuaries would reflect the change in N sources as N loads increase, as well as the change in composition of primary producers. The logarithmic response by $\delta^{15}\text{N}$ in seston and sediment may reflect the combination of these two effects.

The rates at which $\delta^{15}\text{N}$ values in near-bottom seston and surface sediment responded to increasing N load or to increasing percentage wastewater were not significantly different (Fig. 2A,B, test for homogeneity of slopes [Sokal and Rohlf 1981], N load, $F_{1,12} = 0.10$, $p = 0.75$; percentage wastewater, $F_{1,12} = 0.29$, $p = 0.60$). The y intercepts of each regression, however, differed between seston and sediment (analysis of covariance, N load, $F_{1,13} = 9.34$, $p = 0.01$; percentage wastewater, $F_{1,13} = 15.73$, $p = 0.002$), driven by the consistently heavier N isotopic signatures of seston. These results demonstrate that $\delta^{15}\text{N}$ in seston and sediment responded similarly to increasing N load across the eight estuaries, but the magnitude of response was consistently greater in seston compared with sediment.

$\delta^{13}\text{C}$ values in seston and sediment were independent of N-loading rate or percentage contribution of wastewater (Fig. 2C,D) but reflected sources of organic matter available in the different estuaries, with $\delta^{13}\text{C}$ in seston significantly ($t = 2.5$, $p = 0.03$, $df = 13$) lighter than in sediment (Fig. 2C,D). $\delta^{13}\text{C}$ values ranged from -16‰ to -21‰ in sediment (Fig. 2C,D), which suggests sediments were comprised primarily of marsh-derived and benthic microalgal sources (Peterson and Fry 1987; Currin et al. 1995; Cloern et al. 2002). $\delta^{13}\text{C}$ values in seston ranged from -18‰ to -24‰ (Fig. 2C,D), reflecting marine phytoplankton and freshwater sources (Peterson and Fry 1987; Currin et al. 1995; Cloern et al. 2002). One estuary in particular, Weweantic River (WR, Table 1), bore primarily freshwater-derived $\delta^{13}\text{C}$ signatures (Fig. 2C,D). These data suggest C composition differed between near-bottom seston and surface sediment, but $\delta^{13}\text{C}$ in seston and sediment responded similarly to these changes across estuaries, with the magnitude of response greater in sediment than seston.

Cape Cod $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ values compared with other sites—To determine whether the biogeochemical relationships we observed between near-bottom seston and surface sediment occur in other systems, we compared our results with pair-wise comparisons of seston and sediment for $\delta^{15}\text{N}$ (Fig. 3A) and $\delta^{13}\text{C}$ (Fig. 3B) values reported in the literature. To perform these analyses, we compared our data with a detailed literature review of $\delta^{15}\text{N}$ in estuarine seston and sediments (Fig. 3A; Owens 1987) and to more recent studies where both seston and surface sediments were collected at common locations in relatively shallow estuaries by methods similar to ours (Fig. 3, "Other studies"). Where possible, we limited our comparison to studies that reported spring and summer or year-round mean values because we collected

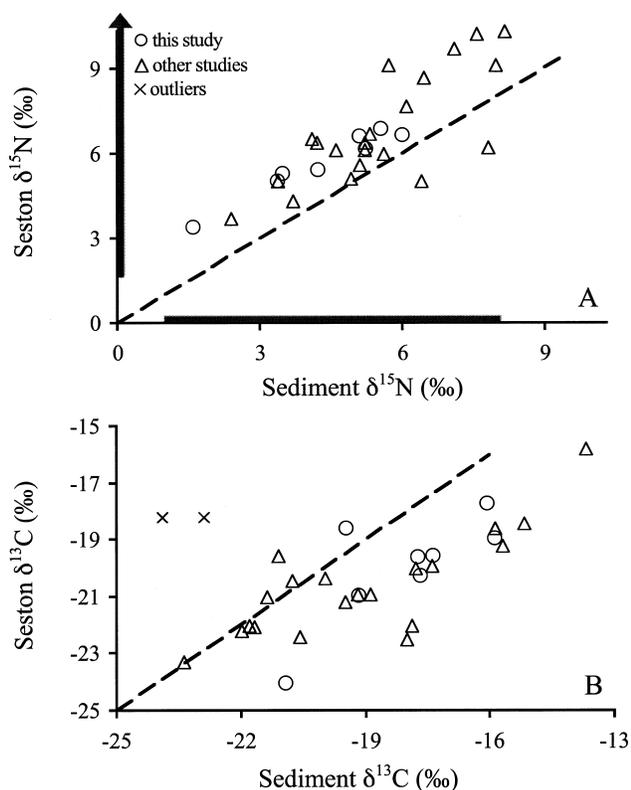


Fig. 3. (A) Mean $\delta^{15}\text{N}$ values in seston plotted versus $\delta^{15}\text{N}$ in sediment and (B) mean $\delta^{13}\text{C}$ in seston versus $\delta^{13}\text{C}$ in sediment for this study and others where ratios of both isotopes were measured for seston and surface sediment in the same location. Data from Delaware Bay, Delaware (Cifuentes et al. 1989); Waquoit Bay, Massachusetts (McClelland and Valiela 1998b); Las Palles, France (Riera 1998); Oosterschelde, the Netherlands (Riera et al. 2002); Lake of Sabaudia, Italy (Vizzini and Mazzola 2003); Pleasant Bay, Massachusetts (Carmichael et al. 2004b). Gray bars (A) show the range of $\delta^{15}\text{N}$ in estuarine seston and sediment among over 100 data points compiled by Owens (1987). Dashed line shows 1:1 correlation. Outliers (Sokal and Rohlf 1981) were not included in the correlation.

our samples in warmer months when sediment $\delta^{15}\text{N}$ values may be light compared with seston (Vizzini and Mazzola 2003). Since most previous studies have not compared bottom-water seston with sediments, we were forced to compare our isotopic data with studies that collected seston at the surface or midwater. This difference, however, provided a serendipitous opportunity to determine the extent to which our results may be generalized to describe biogeochemical coupling between seston and sediment or resulting effects on estuarine food supply elsewhere.

Comparing our data in combination with data from previous studies, $\delta^{15}\text{N}$ values in seston were significantly positively correlated with $\delta^{15}\text{N}$ in surface sediment (Pearson's $r = 0.81$, Fisher's Z test, $p < 0.001$), with a majority of points falling above the line indicating a 1:1 correlation (Fig. 3A). This finding indicates that $\delta^{15}\text{N}$ in seston and sediment increased together across different locations worldwide, but seston values were significantly heavier than sediment. The mean difference between $\delta^{15}\text{N}$ in seston and $\delta^{15}\text{N}$ in sediment among our estuaries ($1.4 \pm 0.2\text{‰}$) was not significantly dif-

ferent from the mean difference ($1.3 \pm 0.3\text{‰}$) measured between seston and sediment from the "other studies" shown in Fig. 3 ($t = 0.23$, $p = 0.82$, $df = 27$). The gray bars in Fig. 3 show the range of $\delta^{15}\text{N}$ signatures in seston and sediment compiled by Owens (1987). Our estuaries and those with which we compared our data were representative of this range of $\delta^{15}\text{N}$ signatures sampled broadly.

$\delta^{13}\text{C}$ values in seston were also significantly positively correlated with $\delta^{13}\text{C}$ in sediment for the combination of our data and other studies (Pearson's $r = 0.78$, Fisher's Z test, $p < 0.001$), with the majority of points falling below the 1:1 line (Fig. 3B), indicating $\delta^{13}\text{C}$ in sediment was typically heavier than seston. As with $\delta^{15}\text{N}$, the mean difference between $\delta^{13}\text{C}$ in seston and $\delta^{13}\text{C}$ in sediment among the Cape Cod estuaries we sampled ($1.9 \pm 0.4\text{‰}$) was not significantly different from the differences measured among other studies ($1.5 \pm 0.4\text{‰}$, $t = 0.53$, $p = 0.52$, $df = 28$).

Overall, there were well-defined relationships between increasing isotopic signatures in seston and sediment among Cape Cod estuaries that were shared by similar data from other studies (Fig. 3). As in Cape Cod estuaries, data from other estuaries suggest seston and sediment changed together, but, on average, seston $\delta^{15}\text{N}$ values were heavier and $\delta^{13}\text{C}$ values were lighter compared with sediment (Fig. 3). These isotopic comparisons show that there is a degree of coupling between seston and sediment and that there also are consistent differences. The implications of this coupling on estuarine food supply are twofold. First, since isotopic signatures in seston and sediment changed together, foods available to consumers from seston and sediment may change concomitantly as N loads to estuaries increase. Second, the consistent differences in magnitude of isotopic signatures between seston and sediment suggest differences in composition that may make near-bottom seston and surface sediment predictably distinguishable in coastal food webs.

Accordingly, lighter $\delta^{15}\text{N}$ and heavier $\delta^{13}\text{C}$ values in surface sediment compared with near-bottom seston could result from the lighter $\delta^{15}\text{N}$ and heavier $\delta^{13}\text{C}$ values typical of benthic microalgae compared with phytoplankton (Currin et al. 1995; Cloern et al. 2002) and associated with detritus (Currin et al. 1995), which may settle and continue to decompose in sediments. Alternatively, a greater influence of freshwater sources on seston compared with sediment could also influence the pattern of isotopic signatures since terrigenous sources and freshwater phytoplankton convey lighter $\delta^{13}\text{C}$ and heavier $\delta^{15}\text{N}$ (Owens 1987; Cloern et al. 2002). Examining specific aspects of seston and sediment composition relative to physical and biological features of each estuary provides data to test these notions.

Seston and sediment composition—To determine aspects of composition that accounted for the biogeochemical coupling between seston and sediment, discern how this coupling was mediated by other estuarine features, and better define effects on estuarine food supply, we compared changes in seston and sediment composition with other estuarine features across estuaries.

Microalgae—Chl *a* concentration in seston and sediment increased significantly with increasing N load (Fig. 4A,C),

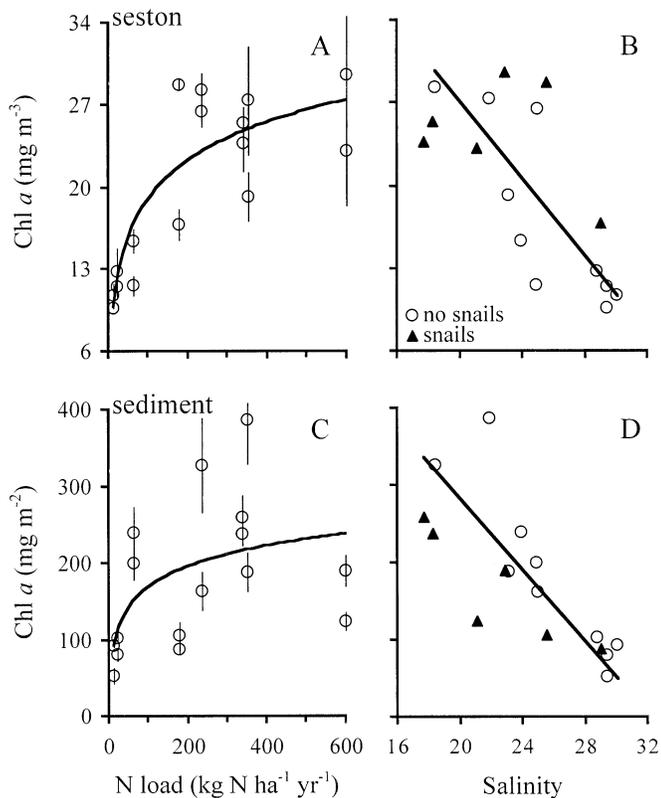


Fig. 4. Mean (\pm standard error) Chl *a* concentration in seston (A and B) and sediment to a depth of 3 cm (C and D) compared with N-loading rate to the watersheds of eight Cape Cod estuaries (A and C) (seston, $y = 4.71 \ln x - 2.68$, $r^2 = 0.74$, $F_{15} = 39.72$, $p < 0.001$; sediment, $y = 38.77 \ln x - 9.58$, $r^2 = 0.30$, $F_{15} = 6.02$, $p = 0.03$), and compared with mean salinity (B and D) at two sites within each estuary (type II regression yielded best-fit lines for seston, $y = -1.79x + 64.06$, $r^2 = 0.50$, $F_{15} = 13.73$, $p = 0.002$; and sediment, $y = -23.16x + 746.22$, $r^2 = 0.68$, $F_{15} = 29.97$, $p < 0.001$). Snails = *N. obsoletus* (Table 1).

which suggests that higher N loads increased phytoplankton and benthic microalgal production in the nearshore areas we sampled. The rate of Chl *a* increase with N enrichment decreased at higher loads (Fig. 4A,C), generating a logarithmic relationship. Similar logarithmic responses to increased N loading have been measured in terms of phytoplankton production across many marine water bodies (Borum 1996). The logarithmic response of Chl *a* to increasing N loads may result from microalgae reaching their physiological capacity to use N for growth or self-shading as they proliferate (Oviatt et al. 1989; Valiela et al. 1992; Borum 1996). These data indicate microalgal biomass increased together in seston and sediment as N loads increased across estuaries.

Relationships between Chl *a* and N load were much more variable for sediment than seston (Fig. 4C), with Chl *a* concentrations in sediment lowest among estuaries of highest salinity and among sites where grazers (*Nassarius obsoletus*) were present (Fig. 4C,D, and Table 1). Chl *a* concentration in seston and sediment decreased significantly with increasing salinity (Fig. 4B,D). The presence of benthic grazers did not affect Chl *a* concentration in seston (Fig. 4B). In sedi-

ment, however, all but one site where grazers were found (Table 1) fell below the regression line comparing Chl *a* concentration with salinity (Fig. 4D), indicating Chl *a* concentrations at these sites were lower than expected if no grazers were present. In fact, salinity and the presence of grazers accounted for more of the variation in Chl *a* concentration in sediments ($r^2 = 0.68$, Fig. 4D) than N loads alone ($r^2 = 0.30$, Fig. 4C), while in seston N-loading rates alone accounted for most of the variation (Fig. 4B). These findings suggest higher salinity and the presence of grazers limited microalgal biomass in sediment of some estuaries and, in part, mediated sediment composition.

Among the estuaries we sampled, larger N loads were found in locations with lower mean salinity (Table 1, $r = -0.67$, Fisher's Z test, -2.94 , $p = 0.003$). This finding was not surprising since land-derived N loads are transported to Cape Cod estuaries by freshwater (Valiela et al. 1992), and $\delta^{13}\text{C}$ signatures in seston suggested freshwater inputs were substantial in some estuaries (Fig. 2B). Salinity, therefore, may be related to the total amount of N available to producers at each site and may account for relationships between Chl *a* and salinity (Fig. 4B,D). Review of the literature reveals no clear pattern between salinity and Chl *a* concentration in sediment across estuarine systems throughout the world (Köster et al. 1997; Hopkinson et al. 1999; Thornton et al. 2002). Salinity (within the range we measured) may be an estuary-specific feature that did not have a major effect on the overall coupling of seston and sediment composition in nearshore areas of these estuaries.

Despite the potentially limiting effects of grazer abundance and associated with increased salinity at some sites, higher concentrations of Chl *a* were found at higher N loads (Fig. 4A,C), with Chl *a* concentrations 4–17 times higher in sediment than seston (Fig. 4A,C). In fact, Chl *a* concentrations in Cape Cod estuaries were within, but at the high end of, the range of Chl *a* concentrations found in seston and sediment worldwide (Lukatelich and McComb 1986; Valiela et al. 1992; Cebrián and Valiela 1999), and higher microalgal biomass in sediment compared with seston is common among coastal estuaries (Granéli and Sundbäck 1985; Lukatelich and McComb 1986; MacIntyre and Cullen 1995). Such high Chl *a* concentrations indicate that the limiting effects of high salinity and the presence of grazers were likely minor compared with production stimulated by N enrichment.

The significantly positive effect of N enrichment on phytoplankton and benthic microalgae biomass has important implications for estuarine food supply and biogeochemistry at the sediment–water interface of shallow coastal estuaries. First, increased microalgal biomass may increase the quantity of food available to primary consumers by increasing the organic load from microalgal particles and inevitably their detritus (Smaal et al. 1986; Fegley et al. 1992). Second, these changes may affect production-driven biogeochemistry (Risgaard-Petersen 2003; Tobias et al. 2003), potentially having the greatest effect on sediment processes since N-stimulated microalgal concentrations were relatively higher in sediments than seston. Third, by increasing microalgal biomass in seston and sediment, N enrichment may also alter C and N content, changing the quality of foods available to

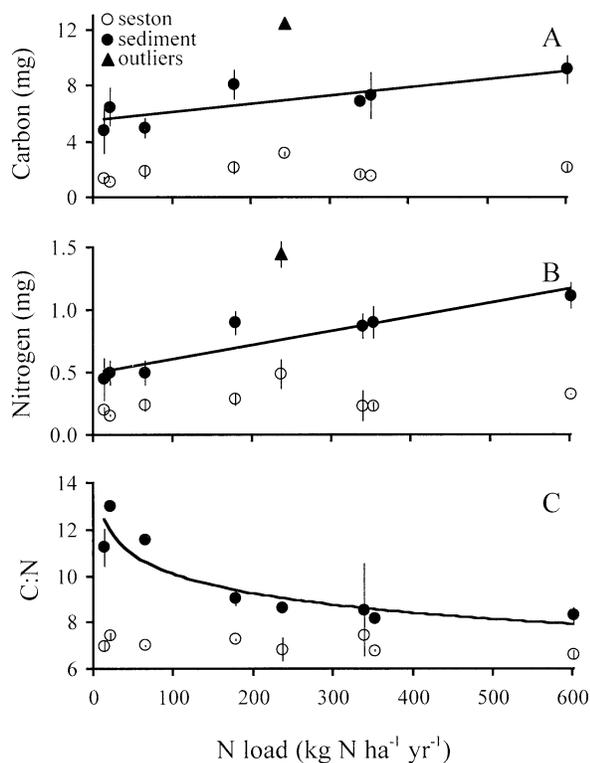


Fig. 5. Mean (\pm standard error) concentration of (A) carbon and (B) nitrogen in seston (L^{-1}) and sediment (g^{-1}) and (C) C:N compared with N-loading rates to the watersheds of eight Cape Cod estuaries. Outliers to the regression were determined by calculating standardized residuals according Sokal and Rohlf (1981) and were not included in regression analyses (sediment [A] $y = 0.01x + 5.50$, $r^2 = 0.67$, $F_6 = 10.22$, $p = 0.02$ [B] $y = 0.001x + 0.50$, $r^2 = 0.87$, $F_6 = 33.70$, $p = 0.002$ [C] $y = -1.21 \ln x + 15.66$, $r^2 = 0.83$, $F_7 = 29.17$, $p = 0.002$).

consumers and the abundance of C and N contributing to isotopic signatures from these sources. We related seston–sediment coupling, reflected in isotopic signatures, to the quality of benthic food resources by assessing C and N composition of seston and sediment.

Carbon and nitrogen concentrations—C and N concentrations in surface sediment increased significantly with increasing N load to the watersheds of eight Cape Cod estuaries (Fig. 5A,B), resulting in a significant decrease in sediment C:N as N loads increased (Fig. 5C). C and N in seston, however, were not significantly influenced by N load. These data point out significant differences in seston and sediment composition that may be related to the consistent differences in isotopic signature across estuaries.

The greater change in sediment C:N compared with seston in response to increasing N loads may have two explanations. First, Chl *a* concentrations were substantially higher in sediment than seston, which suggests that increased microalgal biomass may have accounted for the correspondingly higher C and N content in sediment (Fig. 5A,B). Second, C:N in seston decreased significantly as flushing times increased across estuaries (Fig. 6A). This relationship was highly predictive ($r^2 = 0.88$) and suggests greater possibility

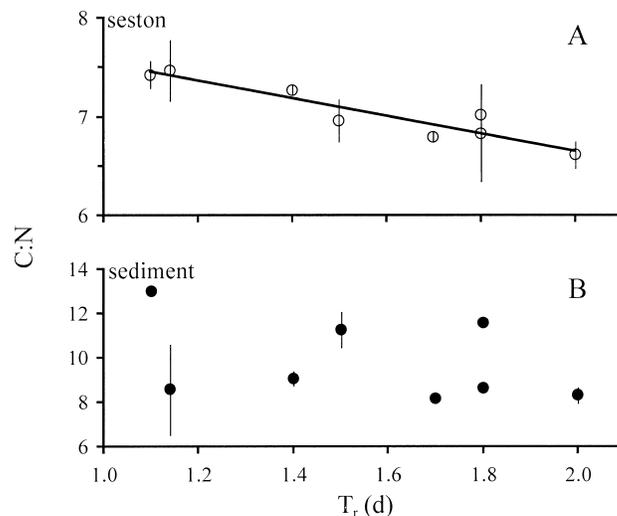


Fig. 6. Mean (\pm standard error) C:N ratio in (A) seston and (B) sediment compared with estuary flushing time (seston, $y = -0.90x + 8.44$, $r^2 = 0.88$, $F_7 = 44.55$, $p < 0.001$).

for net transport of seston particles through and out of the estuary on each tidal cycle compared with sediment (Baillie and Welsh 1980; Snow et al. 2000). Although N enrichment increased microalgal concentration in both seston and sediment, the secondary effects of this increase were better recorded in sediment, potentially explaining how changes in seston and sediment composition may remain coupled, while the magnitude of responses to nutrient enrichment differ. Greater changes in sediment composition in response to increased N enrichment, compared with seston, is contrary to studies suggesting sediments do not reliably reflect N enrichment (Granéli and Sundbäck 1985; Sundbäck et al. 1991) but are consistent with conclusions of Jørgensen (1996), who suggested sediments may be the component of coastal ecosystems most sensitive to eutrophication.

Differences in C and N content between seston and sediment also may affect estuarine food supply. C:N was significantly lower in seston compared with sediment (paired *t*-test, $t = 4.50$, $df = 7$, $p = 0.003$), with the greatest difference among estuaries receiving lower N loads (Fig. 5C). Although Chl *a* concentration and, hence, the quantity of organic particles may have been greater in sediment, these data suggest seston provided higher quality food to the base of the food web, with seston and sediment composition converging in quality as N loads increased (Fig. 5C). Higher C:N in sediment compared with seston is consistent with typically higher C:N ratios in detritus and sedimenting organic matter (Rice and Tenore 1981; Valiela 1995), which suggests that sediment also likely provided different specific sources of N and C to benthic food webs than seston.

Overall, our data suggest the consistent coupling between near-bottom seston and surface sediment composition was most likely driven by differences in type and concentrations of microalgae between seston and sediment. First, benthic microalgae and detritus are typically lighter in $\delta^{15}N$ and heavier in $\delta^{13}C$ compared with phytoplankton (Peterson and Fry 1987; Currin et al. 1995; Cloern et al. 2002), consistent

with the pattern of lighter $\delta^{15}\text{N}$ and heavier $\delta^{13}\text{C}$ signatures found in sediment compared with near-bottom seston across Cape Cod estuaries (Fig. 2) and others (Fig. 3). Second, Chl *a* concentration was the only aspect of composition that, like isotopic signatures, changed concomitantly in seston and sediment across estuaries (Figs. 2 and 4). Third, Chl *a* concentration increased in near-bottom seston and surface sediment despite differences in estuary-specific physical and biological factors such as salinity, abundance of snails, and estuary flushing times (Figs. 5 and 6). Fourth, isotopic signatures in seston and sediment did not show a trend with other variables. For example, although different N inputs conveyed to estuaries by freshwater increased N isotopic ratios in seston and sediment across estuaries (Fig. 2), salinity did not show a trend with isotopic ratios in seston and sediment (Table 1 and Fig. 2). Subsequent changes in N and C composition, SPM, or POM either did not show a trend across estuaries or were discernable only in surface sediment (Table 1 and Figs. 5 and 6), which suggests they were not substantially related to the coupling of seston and sediment composition across locations. These comparisons suggest that microalgal biomass was the component of near-bottom seston and surface sediment substantial enough to be reflected in isotopic ratios.

There are several possible avenues by which increased microalgal biomass could lead to coupling of seston and sediment composition and, in turn, their isotopic ratios. One possibility is through resuspension of benthic microalgae (MacIntyre and Cullen 1995; Lucas et al. 2000). Resuspension, however, would likely vary among different estuaries with different tidal cycles and flushing rates (Baillie and Welsh 1980). While likely contributing to local differences in Chl *a* and organic matter concentrations (Snow et al. 2000), it seems improbable that resuspension was primarily responsible for the consistent differences we demonstrated. Another more likely possibility is coupling through biochemical processes such as the exchange of inorganic nutrients via photosynthesis (Sundbäck et al. 1991; Tobias et al. 2003) or decomposition of organic matter (Hopkinson et al. 1999; Risgaard-Petersen 2003) and diffusion of organic nutrients by microbes under anoxic conditions (Vallino et al. 1996), all of which are related to microalgal biomass. Seston and sediments in our estuaries likely provided a substantial opportunity for such biogeochemical exchanges, since microalgal production was high compared with estuaries worldwide, and sediments maintained isotopic values and C:N reflective of detritus and bacterial decomposition.

Seston–sediment coupling has definite implications for assessing estuarine food supply. First, since seston and sediment responded similarly to increased N enrichment in terms of primary production, the quantity of particles available to consumers from these sources likely increased together. The composition of those particles, however, differed between seston and sediment. These differences mean that seston and sediment ultimately may provide different quantity and quality foods to estuarine benthic consumers (Kang et al. 2003; Carmichael et al. 2004b) but that these features may change together among different estuaries. Second, the advantage of these differences is that they were reflected as consistent differences in stable isotopic composition that help make

seston and sediment distinguishable in food webs (Carmichael et al. 2004b). Thus, although seston and sediment composition is coupled, each may remain a distinct component of benthic food webs.

This study is the first to our knowledge to compare and contrast composition of near-bottom seston and surface sediment in tandem, describing coupling of seston and sediment composition and implications for estuarine food supply and biogeochemistry across estuaries receiving different N loads. Comparison of our results with studies that sampled during roughly the same times during the year, by methods similar to ours, likely reduced variation sufficiently to detect the coupling of near-bottom seston and sediment composition indicated by isotopic ratios in seston and sediment. Consistent relationships between seston and sediment isotopic composition across widely distributed estuaries suggests this coupling may be relatively independent of estuary-specific physical features. We cannot be certain to what extent specific features of near-bottom seston and surface sediment composition measured during this study may be applied more broadly to assessing relationships between seston and sediment estuary-wide, since we sampled within nearshore areas of each estuary. Our data, however, provide evidence that coupling of seston and sediment composition may exist in shallow areas of estuaries worldwide.

References

- BAILLIE, P., AND B. WELSH. 1980. The effect of tidal resuspension on the distribution of intertidal epipelagic algae in an estuary. *Estuar. Coast. Mar. Sci.* **10**: 165–180.
- BORUM, J. 1996. Shallow waters and land/sea boundaries, pp. 179–203. *In* B. Jørgensen and K. Richardson [eds.], *Eutrophication in coastal marine ecosystems*. Coastal and estuarine studies. American Geophysical Union.
- CAHOON, L., J. NEARHOOF, AND C. TILTON. 1999. Sediment grain size effect on benthic microalgal biomass in shallow aquatic ecosystems. *Estuaries* **22**: 735–741.
- CARMICHAEL, R., B. ANNETT, AND I. VALIELA. 2004a. Nitrogen loading to Pleasant Bay, Cape Cod: Application of models and stable isotopes to detect incipient nutrient enrichment of estuaries. *Mar. Pollut. Bull.* **48**: 137–143.
- , D. RUTECKI, B. ANNETT, E. GAINES, AND I. VALIELA. 2004b. Position of horseshoe crabs in estuarine food webs: N and C stable isotopic study of foraging ranges and diet composition. *J. Exp. Mar. Biol. Ecol.* **299**: 231–253.
- CEBRIÁN, J., AND I. VALIELA. 1999. Seasonal patterns in phytoplankton biomass in coastal ecosystems. *J. Plankton Res.* **21**: 429–444.
- CIFUENTES, L., J. SHARP, AND M. FOGEL. 1988. Stable carbon and nitrogen isotope biogeochemistry in the Delaware estuary. *Limnol. Oceanogr.* **33**: 1102–1115.
- CLOERN, J. 2001. Our evolving conceptual model of the coastal eutrophication problem. *Mar. Ecol. Prog. Ser.* **210**: 223–253.
- , E. CANUEL, AND D. HARRIS. 2002. Stable carbon and nitrogen isotope composition of aquatic and terrestrial plants of the San Francisco Bay estuarine system. *Limnol. Oceanogr.* **47**: 713–729.
- COLE, M., AND OTHERS. 2004. Assessment of a $\delta^{15}\text{N}$ isotopic method to indicate anthropogenic eutrophication in aquatic ecosystems. *J. Environ. Qual.* **33**: 124–132.
- CURRIN, C., S. NEWELL, AND H. PAERL. 1995. The role of standing dead *Spartina alterniflora* and benthic microalgae in salt marsh

- food webs: Considerations based on multiple stable isotope analysis. *Mar. Ecol. Prog. Ser.* **121**: 99–116.
- FEGLEY, S., B. MACDONALD, AND T. JACOBSEN. 1992. Short-term variation in the quantity and quality of seston available to benthic suspension feeders. *Estuar. Coast. Shelf Sci.* **34**: 393–412.
- GRANÉLI, E., AND K. SUNDBÄCK. 1985. The response of planktonic and microbenthic algal assemblages to nutrient enrichment in shallow coastal waters, southwest Sweden. *J. Exp. Mar. Biol. Ecol.* **85**: 253–268.
- HOPKINSON, C., JR., A. GIBLIN, J. TUCKER, AND R. GARRITT. 1999. Benthic metabolism and nutrient cycling along an estuarine salinity gradient. *Estuaries* **4**: 863–881.
- JØRGENSEN, B. 1996. Material flux in the sediment, pp. 115–135. *In* B. Jørgensen and K. Richardson [eds.], *Eutrophication in coastal marine ecosystems*. Coastal and estuarine studies. American Geophysical Union.
- KANG, C., J. KIM, K. LEE, J. KIM, P. LEE, AND J. HONG. 2003. Trophic importance of benthic microalgae to macrozoobenthos in coastal bay systems in Korea: Dual stable C and N isotope analysis. *Mar. Ecol. Prog. Ser.* **259**: 79–92.
- KÖSTER, M., S. DAHLKE, AND L. MEYER-REIL. 1997. Microbiological studies along a gradient of eutrophication in a shallow coastal inlet in the Southern Baltic Sea (Nordugensche Boden). *Mar. Ecol. Prog. Ser.* **152**: 27–39.
- KROEGER, K., J. BOWEN, D. CORCORAN, J. MOORMAN, J. MICHALOWSKI, C. ROSE, AND I. VALIELA. 1999. Nitrogen loading to Green Pond, Falmouth, MA: Sources and evaluation of management options. *Environ. Cape Cod* **2**: 15–26.
- , M. COLE, J. YORK, AND I. VALIELA. *In press*. N transport to estuaries in wastewater plumes: Modeling and isotopic approaches. *Groundwater*.
- LAKE, J., R. MCKINNEY, F. OSTERMAN, R. PRUELL, J. KIDDON, S. RYBA, AND A. LIBBY. 2001. Stable nitrogen isotopes as indicators of anthropogenic activities in small freshwater systems. *Can. J. Fish. Aquat. Sci.* **58**: 870–878.
- LORENZEN, C. 1967. Determination of chlorophyll and pheo-pigments: Spectrophotometric equations. *Limnol. Oceanogr.* **12**: 343–346.
- LUCAS, C., J. WIDDOWS, M. BRINSLEY, S. SALKELD, AND P. HERMAN. 2000. Benthic-pelagic exchange of microalgae at a tidal flat. 1. Pigment analysis. *Mar. Ecol. Prog. Ser.* **196**: 59–73.
- LUKATELICH, R., AND A. MCCOMB. 1986. Distribution and abundance of benthic microalgae in a shallow southwestern Australian estuarine system. *Mar. Ecol. Prog. Ser.* **27**: 287–297.
- MACINTYRE, H., AND J. CULLEN. 1995. Fine-scale vertical resolution of chlorophyll and photosynthetic parameters in shallow-water benthos. *Mar. Ecol. Prog. Ser.* **122**: 227–237.
- MAYER, B., AND OTHERS. 2002. Sources of nitrate in rivers draining sixteen watersheds in the northeastern U.S.: Isotopic constraints. *Biogeochemistry* **57/58**: 171–197.
- MCCLELLAND, J., AND I. VALIELA. 1998a. Changes in food web structure under the influence of increased anthropogenic nitrogen inputs to estuaries. *Mar. Ecol. Prog. Ser.* **168**: 259–271.
- , AND ———. 1998b. Linking nitrogen in estuarine producers to land-derived sources. *Limnol. Oceanogr.* **43**: 577–585.
- MICHENER, R., AND D. SCHELL. 1994. Stable isotope ratios as tracers in marine aquatic food webs, pp. 138–157. *In* K. Lajtha and R. H. Michener [eds.], *Stable isotopes in ecology and environmental science*. Blackwell Scientific Publications.
- OVIATT, C., P. LANE, F. FRENCH, AND P. DONAGHAY. 1989. Phytoplankton species and abundance in response to eutrophication in coastal marine mesocosms. *J. Plankton Res.* **11**: 1223–1244.
- OWENS, N. 1987. Natural variations in ^{15}N in the marine environment, pp. 408–416. *In* J. H. S. Blaxter and A. J. Southward [eds.], *Advances in marine biology*. Academic Press.
- PETERSON, B., AND B. FRY. 1987. Stable isotopes in ecosystem studies. *Annu. Rev. Ecol. Syst.* **18**: 293–320.
- RICE, D., AND K. TENORE. 1981. Dynamics of carbon and nitrogen during the decomposition of detritus derived from estuarine macrophytes. *Estuar. Coast. Shelf Sci.* **13**: 681–690.
- RIERA, P. 1998. $\delta^{15}\text{N}$ of organic matter sources and benthic invertebrates along an estuarine gradient in Marennes-Oleron Bay (France): Implications for the study of trophic structure. *Mar. Ecol. Prog. Ser.* **166**: 143–150.
- , L. J. STAL, AND J. NIEUWENHUIZE. 2002. $\delta^{13}\text{C}$ versus $\delta^{15}\text{N}$ of co-occurring molluscs within a community dominated by *Crassostrea gigas* and *Crepidula fornicata* (Oosterschelde, The Netherlands). *Mar. Ecol. Prog. Ser.* **240**: 291–295.
- RISGAARD-PETERSEN, N. 2003. Coupled nitrification-denitrification in autotrophic and heterotrophic estuarine sediments: On the influence of benthic microalgae. *Limnol. Oceanogr.* **48**: 93–105.
- SMAAL, A., J. VERHAGEN, J. COOSEN, AND H. HAAS. 1986. Interaction between seston quantity and quality and benthic suspension feeders in the Oosterschelde, the Netherlands. *Ophelia* **26**: 385–399.
- SNOW, G., J. ADAMS, AND G. BATE. 2000. Effect of river flow on estuarine microalgal biomass and distribution. *Estuar. Coast. Shelf Sci.* **51**: 255–266.
- SOKAL, R., AND F. ROHLF. 1981. *Biometry*. W. H. Freeman and Company.
- SUNDBÄCK, K., V. ENOKSSON, W. GRANÉLI, AND K. PETERSSON. 1991. Influence of sublittoral microphytobenthos on the oxygen and nutrient flux between sediment and water: A laboratory continuous-flow study. *Mar. Ecol. Prog. Ser.* **74**: 263–279.
- THORNTON, D., L. DONG, G. UNDERWOOD, AND D. NEDWELL. 2002. Factors affecting microphytobenthic biomass, species composition and production in the Colne Estuary (UK). *Aquat. Microb. Ecol.* **27**: 285–300.
- TOBIAS, C., A. GIBLIN, J. MCCLELLAND, J. TUCKER, AND B. PETERSON. 2003. Sediment DIN fluxes and preferential recycling of benthic microalgal nitrogen in a shallow macrotidal estuary. *Mar. Ecol. Prog. Ser.* **257**: 25–36.
- VALIELA, I. 1995. *Marine ecological processes*, 2nd ed. Springer-Verlag.
- , J. BOWEN, AND K. KROEGER. 2002. Assessment of models for estimation of land-derived nitrogen loads to shallow estuaries. *Appl. Geochem.* **17**: 935–953.
- , M. GEIST, J. MCCLELLAND, AND G. TOMASKY. 2000. Nitrogen loading from watersheds to estuaries: Verification of the Waquoit Bay nitrogen loading model. *Biogeochemistry* **49**: 277–293.
- , AND OTHERS. 1992. Couplings of watersheds and coastal waters: Sources and consequences of nutrient enrichment in Waquoit Bay, Massachusetts. *Estuaries* **15**: 443–457.
- , AND OTHERS. 1997. Nitrogen loading from coastal watersheds to receiving estuaries: New method and application. *Ecol. Appl.* **7**: 358–380.
- VALLINO, J., C. HOPKINSON, AND J. HOBBIIE. 1996. Modeling bacterial utilization of dissolved organic matter: Optimization replaces monod growth kinetics. *Limnol. Oceanogr.* **41**: 1591–1609.
- VIZZINI, S., AND A. MAZZOLA. 2003. Seasonal variations in the stable carbon and nitrogen isotope ratios ($^{13}\text{C}/^{12}\text{C}$ and $^{15}\text{N}/^{14}\text{N}$) of primary producers and consumers in a western Mediterranean coastal lagoon. *Mar. Biol.* **142**: 1009–1018.
- WENTWORTH, C. 1922. A scale of grade class terms for clastic sediments. *J. Geol.* **30**: 377–392.
- ZIMMERMAN, A., AND E. CANUEL. 2001. Bulk organic matter and lipid biomarker composition of Chesapeake Bay surficial sediments as indicators of environmental processes. *Estuar. Coast. Shelf Sci.* **53**: 319–341.

Received: 22 December 2003

Accepted: 30 August 2004

Amended: 14 September 2004