microfossils (benthic foraminifera and ostracods), pollen and seeds, chemical fingerprints (stable isotopes, lipid biomarker compounds and black carbon), and mollusk shells preserved in sediment core records.

Keywords Chesapeake Bay • Paleoecology • Biomarkers • Mollusks • Microfossils • Pollen • Lipid biomarkers • Eutrophication

1 Background

Chesapeake Bay, the largest estuary in the United States, is a complex ecosystem with a long historical record of human habitation within its watershed, providing a good model system for understanding how climate, anthropogenic activities and the environment interact (Fig. 1). The mid-Atlantic region now occupied by the Bay and adjacent coastal plain was inundated during global warmth of the Pliocene (4.5–2.8 million years ago, Ma) by sea level extending more than 100 km inland (Dowsett and Cronin 1989; Hobbs 2004). During the mid-late Quaternary, the last ~500 kiloannum (500 ka), the region was repeatedly inundated during interglacial periods of low polar ice volume and high global sea level (Colman and Mixon 1988). During glacial periods, when global sea level was 125 m below its current level, the Bay region was a channel and floodplain habitat experiencing fluvial erosion and deposition. More generally, climate exerted a strong influence on the Bay's

m belojzel extending more than periods of low po al.aternary, th). Bac(oasogenic5(f/GShte, anthr periods of low po ()dly inunda

periods of lo the last ~500 oannum (500

~500 ki1aoannum (500 periods of lo14.3s59999Tw-4.84



fertilizers were first introduced following World War I but their use was interrupted during World War II (Stevenson et al. 1999

rates at depths immune from severe disturbance, the preservation potential of different proxies and the availability of reliable chronologies must be given consideration. This will be discussed later in the chapter.

2 Fossil Pollen and Seeds

Fossil pollen and seeds preserved in sediments deposited in the Chesapeake estuary as well as its tributaries and wetlands have been used to reconstruct the composition of forests and wetlands that inhabited the Chesapeake drainage area over the last 2–14 ka. Different cores span various periods of time, depending on the age of the depositional basin and sedimentation rates, which vary from one locality to another and are related to local land use and the hydrodynamics of the different tributaries. Fossil pollen and seed records in the area of the Chesapeake document climate change through the Holocene consistent with similar records from eastern North America, as well as post-colonial land-use change consistent with regional historical records.

r

•

The majority of sediment cores used for pollen studies were collected using a handoperated piston corer. The cores are typically 5.4 or 6.6 cm in diameter and range in length from 0.3 to 2 m. The sediment cores are transported from the field in their plastic liners to the laboratory where they are stored at 4 °C until extruded. Once extruded from the liner, each core is split in half lengthwise, visually described and cut into 1- or 2-cm samples; one sample is used for seed analysis and the other for pollen analysis and dating. Samples are sealed in labeled ziploc bags and stored at 4 °C until analyzed. Details of the methods used for pollen analysis are provided in Ellison (2017) and can be found in references citing the work of Brush and colleagues found at the end of this chapter.

Sediment layers within cores are dated by identifying the earliest agricultural horizon, recognized by a significant increase in ragweed pollen, and by radiocarbon dating from one to a few horizons below the ragweed agricultural horizon (Brush 1984Ellison (

Date of horizon	Change in vegetation/land use	Pollen indicator
1930 (1923-1932)	Demise of chestnut	Decrease in chestnut pollen to <1 %
1910 (1908–1912)	Decline of chestnut (disease)	Decrease in chestnut pollen
1840 (1820-1860) or 1780 (1760-1800) depending on location	40-50% of land cleared	Ragweed >10%; ratio of oak to ragweed >1 to <5
1730 (1720–1740) or 1650 (1640–1660)	<20% of land cleared	Ragweed >1% to <10%; oak to ragweed ratio >1 to <5
Pre-European	Native American agriculture	Ragweed <1 % or 0

Table 1 Pollen horizons used to date sediment cores

Table 2 Pollen concentration-derived chronology of a portion of a core collected in 1980 and sampled in 2 cm intervals. Dates are provided in Common Era (CE)

Depth (cm)	Sedimentation Rate (cm yr ¹)	Number of years	Chronology (CE)
0-2	0.96	2.1	1980-1978
2-4	1.2	1.7	1978-1976
4-6	0.98	2.0	1976-1974
6-8	0.79	2.5	1974-1972
100-102	0.39	5.1	1848–1843
102-104	0.58	3.4	1843-1849
192-194	0.05	40	335-295
194-196	0.07	28.6	295-266
196-198	0.05	40	266-226

$R_{01} = (n / n_{01})R$, where

R = d/t = average sedimentation rate between two dated horizons,

n = average pollen concentration between two dated horizons,

 n_{0-1} = pollen concentration in an individual sample,

d = depth,

t = number of years between dated horizons.

Chronologies for the cores are estimated by dividing the sedimentation rate by the depth of the sample which gives the number of years represented in each sample (Table 2).



Pollen and seed analyses of sediment cores show the effect of climate and post-European land use in the region of the Chesapeake. Cores collected from three areas differing in soil type and modern vegetation associations show that changes due to climate were synchronous at all sites but differed in composition across sites (Table 3). $\begin{array}{cccc} V & r & C \\ r & \downarrow \not \downarrow E & n \end{array}$

Diagrams of two fossil pollen/seed profiles illustrate the changes that have occurred in Maryland's forests and wetlands over centuries to millennia (Figs. 3 and 4

•







marily a wintertime atmospheric-ocean oscillation in the North Atlantic and Arctic region and is measured by atmospheric pressure changes over Iceland and the Azores (Hurrell et al. 2003). Generally, a positive NAO index leads to relatively warm and wet conditions over the mid-Atlantic region such as occurred from 1970 until the mid-1990s. A negative NAO index results in cool, dry conditions such as those during the 1950s and 1960s.

Calcareous microfossils have been the primary tool used to reconstruct decadal to centennial scale patterns of Bay salinity and temperature associated with modes of climate variability. Proxies used to reconstruct salinity include benthic foraminiferal assemblages (Cronin et al. 2000) and stable isotope geochemistry of shells of the foraminifera *Elphi* ium (Cronin et al. 2005; Saenger et al. 2006). Water temperature is reconstructed using magnesium/calcium (Mg/Ca) ratios in the ostracod oxoconcha (Cronin et al. 2003a). Regional climate during the early part of what is called the Medieval Warm Period (see Fig. 5) was relatively warm and dry, with major periods of dry climate corresponding to continental scale "megadroughts" (Cronin et al. 2005). The Little Ice Age (LIA; 1400–1900 CE; Fig. 5) was relatively cool and wet but experienced extremes in precipitation including 60-70 quasi-cyclic patterns in Bay salinity. Based on comparison of early and late Holocene regional climate, Cronin et al. (2005) and Saenger et al. (2006) showed that early Holocene climate in the mid-Atlantic regions was extremely dry and relatively invariant. They hypothesized that these differences were the result of large-scale changes in atmospheric circulation, notably shifts in the mean position of the Intertropical Convergence Zone and Hadley cell circulation known from proxy records in the tropics and extratropical regions. Knowledge of these climate patterns provides important baseline information about the possible response of the estuary to future climate changes.

С

Rising sea level is one of the greatest threats to Chesapeake Bay due to the low elevation and susceptibility to submergence of large tidal marshes on the eastern shore and, to a lesser degree, parts of the Bay's western coast. The modern Bay and its large tributaries are themselves the products of the drowning of paleo-river valleys that formed during low global sea level during the last glacial period (80–21 ka) and became submerged during the last deglaciation (21–7 ka) (Bratton et al. 2003a). In the case of Chesapeake Bay, regional sea level rise (SLR) is almost double the mean rate of global sea level change during the past century because of land subsidence. This high rate of SLR is due to the region's location adjacent to the southern



Fig. 5 Comparison of paleosalinity from foraminiferal oxygen and carbon isotopes and Mg/ Ca-based paleotemperature records from Chesapeake Bay cores MD2209 and RD-98 modified from Cronin et al. (2003a, b, 2005)). Figure shows drier and warmer early Holocene regional climate compared to conditions during the late Holocene and multi-decadal variability during the last 2000 years including the Medieval Climate Anomaly (also called the Medieval Warm period) and the Little Ice Age formerly glaciated regions have rebounded but the mid-Atlantic region has subsided a total of approximately 8-10 m. This subsidence continues today at a rate of 1.0-1.5 mm year ¹. The combined effect of rising sea level and subsiding land means the current rate of SLR in the bay is about 4 mm per year and this rate is likely to increase in the near future.

A basic question pertaining to SLR and coastal marshes in temperate regions in general, is how does rapidly rising sea level affect marsh ecosystems? Marsh response to SLR varies greatly depending on marsh ecology, climate, hydrology, sediment sources, geomorphology, tidal range, and other factors. In general, during periods of rising sea level, *spartina* marshes typical of Chesapeake Bay can accrete at rates of 1–10 mm per year. At higher rates, marshes usually cannot keep up and drown. Cronin et al. (2007) carried out a detailed analysis of foraminiferal assemblages and stable isotopes from sediment cores that recovered early Holocene marsh deposits. The study focused on the sediments deposited from 9.5 to 7.0 ka, a period that included several abrupt climate oscillations associated with the well-known 8.2 ka cooling event. Sediments, now 20-26 m below modern sea level, recovered from core MD03-2656 located near the boundary between the Bay's mainstem and Pocomoke Sound (Fig. 1), provided the most detailed relative sea level record. Cronin et al. (2007) showed that the Bay was flooded in two abrupt pulses of SLR when marsh foraminiferal species in the Pocomoke region disappeared and marine foraminiferal species became the dominant faunal elements. The foraminiferal data, along with ostracod and pollen evidence, indicated that sea level rose for several centuries at rates at least three times the current rate, with possible brief periods of more rapid rise. The source of melting ice that caused these abrupt sea level rise events was probably the remaining segments of the Laurentide Ice Sheet or portions of the Antarctic Ice Sheet.

Predictions about the rate of future global sea level rise are extremely uncertain due to the complexity and non-linear nature of dynamical processes governing the margins of the Greenland and Antarctic Ice Sheets. Nonetheless, these paleoreconstructions provide definitive evidence that SLR during periods of rapid climatic warming has major ecological impacts on coastal marshes.

r

r

Low levels of dissolved oxygen (DO) and water clarity (turbidity) are two of the most pressing water quality needs in Chesapeake Bay. Ecologically tolerant species of benthic foraminifera and ostracods have been used to reconstruct the timing and nature of changes in DO and turbidity in the main channel of the Bay and the role played by climate and land-use changes. Karlsen et al. (2000) and Cronin and Vann (2003) used benthic foraminifera and ostracods, respectively, to identify when the onset of large-scale human-induced hypoxia occurred in the central part of the mainstem of Chesapeake Bay. Some species of foraminifera (Ammonia parkinsoniana) and ostracods (Cytheromorpha curta) are facultative anaerobes that tolerate

soft-bodied organisms and those with thin, small, high organic content, and aragonitic hard parts are less likely to be preserved than others. Similarly, rare species, and those that inhabit environments with low sedimentation rates, are also less likely to pass through the "taphonomic filter" as the live community is converted into the fossil record. These taphonomic processes are numerous and complex, ranging from chemical dissolution, to mechanical fragmentation, to transport, to bioturbation; many act to decrease the "fidelity" or agreement between the living community and the sedimentary record it produces (Kidwell and Bosence 1991; Behrensmeyer et al. 2000).

Similarly, sedimentary deposits do not represent discrete snapshots or censuses of past communities. Instead, they are time-averaged, meaning that multiple generations of organisms are preserved together in a single stratigraphic unit (Fürsich and Aberhan 1990). Time averaging varies drastically by environment and can range from tens to thousands to millions of years (Martin 1999; Carroll et al. 2003). The overall effect of time averaging is to set limits on temporal resolution by obscuring ecological and environmental change that occurs in fossil assemblages during accumulation (Meldahl et al. 1997). The majority of studies that assess climatic or environmental changes in the Chesapeake Bay ignore the potential for time averaging. assuming either that microfossils and pollen experience little time averaging or that samples have not been significantly reworked based on the quality of their preservation. Field studies, however, suggest that microfossil and pollen time averaging can range from 10 to 10⁴ years (e.g., Martin 1993; Webb 1993; for review see Martin 1999), although these numbers vary considerably according to environment and few estimates of time averaging exist for estuarine settings. Studies that attempt to link fossil preservation to age tend to focus primarily on shallow marine environments and have found that preservation is rarely an indicator of whether or not a specimen has been reworked (Powell and Davis 1990; Flessa et al. 1993; Martin et al. 1996).

Despite the importance of these two factors—preservational bias and time averaging—in potentially undermining the validity of sedimentary data for reconstructing paleoenvironments, few paleoestuarine studies explicitly take them into account. This is extremely unfortunate, given the massive amount of data available on these processes in the paleontological literature (for reviews see Martin 1999; Behrensmeyer et al. 2000) and the ready availability of techniques to specifically address them.

rr

One important metric of preservational bias is the degree to which Holocene assemblages reflect their source communities (i.e., their fidelity) (Behrensmeyer et al. 2000). Compositional fidelity, which focuses on the reliability of species composition, richness, and abundance measures, can be assessed using live-dead comparisons, in which live communities are sampled and compared with death assemblages (Kidwell and Bosence 1991; Kidwell 2001).

С

Lockwood and Chastant (2006; see also Jackson 1968) carried out a live-dead comparison on molluscan assemblages from four sites located in the main channel of the upper Chesapeake Bay. They obtained a total of 3911 mollusk specimens from box-core sampling of the death assemblage (e.g., the dead shells mixed in the several centimeters of sediment below the sediment-water interface). The extent to which death assemblages reflect long-term changes in the live community was assessed using live census data (23,466 molluscan specimens) collected by the Chesapeake Bay Program at the same sites. Fidelity of species composition was assessed by calculating the percentage of: (1) species in the live community found in the death assemblage (live-dead fidelity), (2) species in the death assemblage found in the live community (dead-live fidelity), and (3) individuals in the death assemblage that are represented as species in the live community (following Kidwell and Bosence 1991).

Lockwood and Chastant (2006) documented strong agreement between livecommunity and death-assemblage estimates of molluscan species composition and abundance—77% of the species in the live community were found in the death assemblage, and 99% of the individuals of species found in the death assemblage were found in the live community. Correlations between live and dead estimates of species richness (e.g., number of species) yielded no statistically significant correlations, although correlations did improve with longer-term sampling of the live community. Their study also detailed a strong and significant correlation between rank abundance of taxa in the death assemblage and live rank abundance regardless of the duration of live sampling (Fig. 6). Data on shell mineralogy, shell organic content, and life habit suggested that these factors were not exerting a strong effect on the patterns of rank abundance examined by Lockwood and Chastant (2006).



Fig. 6 Rank abundance of live benthic mollusks in the Chesapeake Bay is significantly correlated with rank abundance of mollusks in the death assemblage (Lockwood and Chastant 2006). This suggests that rank abundance of mollusks is faithfully recorded in the sedimentary record of the bay. Bivariate scatter plots of rank abundance in the live community versus rank abundance in the death assemblage for each species across all sites. Each point in the plot represents a species; trend lines represent least-squares regression lines constrained to pass through the origin (0,0). (a) Data for 1 year of live sampling (R_{24} = 0.68, p = 0.000). 9999961(v)15(e sampling (R)TJ0Tw/GS k2n<</keel/Act2ts0177.000).

512

•

This study indicated that Holocene data can be used, albeit with caution, to reconstruct changes in species composition and community structure through time. For example, if 77% of live species are found in the death assemblage, then a compositional change involving at least 24% of the Holocene fauna through time is unlikely to be driven purely by preservational bias. Similarly, because rank abundance of the live community is statistically significantly correlated with rank abundance of the death assemblage, shifts in rank abundance through time that exceed the variability attributable to taphonomic bias would be considered true ecological signal.

$\lambda_n r C$

Time averaging is defined as the mixing of non-contemporaneous fossil material such that specimens from successive generations, or ecologically unrelated com-

core depths. Ten live shells were also analyzed for AAR to establish an initial D/L value. For more detailed information on the methodology and aminochronological results, see Edwards (2007).

(before the condensed section) ranges from 12 to 900 years, while time averaging in the older part of the core is much larger, ranging from 600 to 2700 years. In addition to this background increase in time averaging, two other intervals in the core show particularly high estimates of time averaging—one peak at 255 cm and another at 1053–1155 cm. This second interval (1100 cm) of the Kent Island core is associated with a condensed section, which is constrained by radiocarbon calibrated dates as between 2.8 and 5.6 ka. To summarize, as one moves to increasingly older and deeper sediments, time averaging and inherent AAR variability increases, limiting temporal resolution of early Holocene deposits. Practically speaking, this means that Chesapeake Bay mollusks may not be particularly useful tools for high-resolution (<500 years) reconstruction of the early Holocene paleoestuarine history—unless one is specifically targeting layers with minimal time averaging. Edwards (2007) argued that estimates of time averaging are likely to be overestimates because they do not adequately compensate for the influences of nonlinear racemization kinetics and inherent variability (i.e., within genus intershell variation).

This combination of high compositional fidelity (Lockwood and Chastant 2006) and high levels of time averaging (Edwards 2007) in Chesapeake Bay molluscan assemblages may seem counterintuitive, but it is a pattern that is being increasingly recognized in coastal ecosystems (e.g., Kidwell et al. 2005). It means that mollusks can provide useful baseline data for ecological restoration and paleoenvironmental reconstruction, but not necessarily at the decadal or centennial timescales that are expected. However, new high-resolution techniques may extend the ability to utilize mollusks for identifying environmental change at shorter timescales. In a recent study, Harding et al. (2010) analyzed oxygen isotopes (δ^{18} O) in vrrmtal change

Given the estimates of preservational bias and time averaging established in previous studies, it is now possible to conduct a preliminary study sampling the Holocene mollusk record of the Chesapeake Bay and examine the potential link between community changes and Holocene environmental changes (see also Arnold 2003). Two Calypso piston cores were collected by the USGS for this study, the Kent Island (MD03-2661) and Parker Creek (MD99-2208) cores (Fig. 1; see papers in Cronin 2000). Detailed information on the Kent Island core is provided above. The Parker Creek core was collected near Parker Creek (38°32.24 N; 76°29.19 W), in 10 m water depth, and reached a core length of 782 cm. Full details of these cores are available at http://geology.er.usgs.gov/eespteam/Atlantic/overview.htm.

Bulk samples of mollusks were collected from 14 depths within the Kent Island core and 9 depths within the Parker Creek core, which produced a total dataset of 33 species and 3410 individuals (Kolbe et al. 2005; Morgan et al. 2005). Shell beds were specifically targeted for this study, since the limited abundance and distribution of molluscan material made it unproductive to sample uniformly throughout the cores. Samples were sieved to 0.5 mm, shell assemblages were sorted, and minimum individuals were counted for each species, from which species richness (e.g., number of species) and rank and proportional abundance were calculated. In order to examine possible links between molluscan community shifts and climate, environmental tolerance data, including salinity, temperature, dissolved oxygen, pH, turbidity, depth, and substrate preferences, were collected for all molluscan species present in the cores. Temporal resolution of all analyses was dictated by the results of Edwards' (2007) time averaging study and, thereby, limited to comparisons of the early Holocene (7.5–6 ka) versus late Holocene (2.3 ka to modern) (e.g., approximately before and after the condensed section in the Kent Island core).

The results for species composition provide a baseline for establishing which species existed in the late Holocene and how this composition relates to modern benthic mollusk communities. Rarefaction analysis (Analytical Rarefaction v1.3, Holland 2003), which involves resampling the data down to progressively smaller sample sizes to explore the effects of sample size on a given metric (Raup 1975), was applied to the results for species richness. In both cores, rarefied data demonstrate the same temporal patterns as raw data—richness appears to be higher in the early Holocene and lower in the late Holocene, although this difference is not statistically significant. This pattern may mirror the modern trend of higher species richness in the high salinity regions of the Bay, since the early Holocene is thought to represent higher salinity conditions.

Species with somewhat higher salinity tolerances (e.g., *ucula proxima* (20–35 ppt), *Fol ia limatula* (18–30 ppt), *Boonea bisuturalis* (18–30 ppt)) were statistically significantly more abundant in the early Holocene and less abundant in the late Holocene (Fig. 8). Molluscan salinity patterns are consistent with past reconstructions based on ostracods, foraminifera, and pollen; all four groups shift from species

indicating drier, warmer (more saline) early Holocene conditions to cooler, wetter (less saline) late Holocene conditions (Cronin and Ishman 2000; Willard and Korejwo 2000). These results are preliminary, but they suggest that: (1) it is possible to use the Holocene record of the Chesapeake Bay as a baseline for ecological restoration and (2) Holocene molluscan assemblages do seem to reflect paleoenvironmental changes, despite the low temporal resolution of the molluscan record.

characterizing changes in sources of carbon over time, as recorded in sediments (Hedges and Parker 1976; Goñi and Thomas 2000; Zimmerman and Canuel 2002). A variety of proxies have been used to trace organic matter sources in Chesapeake Bay including stable carbon and nitrogen isotopes (δ^{13} C and δ^{15} N) and lipid biomarker compounds.

Sediment records of the stable isotopes of carbon and nitrogen (δ^{13} C and δ^{15} N) have provided important insights into changes in algal production, organic matter recycling and nitrogen delivery. However, stable isotopes are best applied when: (a) only a few sources are important and (b) those sources have distinct isotopic signatures. Because these conditions are not typically met in most estuarine and coastal environments (Cloern et al. 2002), organic sources are often better characterized using a combination of molecular biomarkers and bulk stable isotopes, or using more advanced techniques such as compound-specific stable isotope analysis. In recent years, radiocarbon (Δ^{14} C) isotopes have been used as an additional tracer for /8 Tm/Gufor

	Compounds	
Fatty aci biomarkers ^a		
Eubacteria	15:0, i15:0, a15:0, 16:1ω9, i17:0, a17:0, 17:0, 18:1ω7t, 18:1ω5, i19:0, a19:0	
Sulfate-reducing bacteria	i17:1ω7, 10Me16:0, 17:1ω6	
Aerobes	16:1 ω 7, 18:1 ω 7	
Cyanobacteria	Same as eubacteria plus 18:206	
Diatoms	16:1ω3t, 20:5ω3	
ostera marina (seagrass)	5,	
	5,	

Table 4 Examples of lipid biomarkers used in paleoecological studies (adapted from information provided in Killops and Killops (1993), Zimmerman and Canuel (2001) and references therein)

depths of 27, 15 and 8 m, respectively (Fig. 1). The sites were selected to best represent autochthonous sources of OM since they were located downstream of the turbidity maximum and upstream of the Bay mouth. Stable carbon and nitrogen isotopes (δ^{13} C and δ^{15} N) were used to examine changes in C and N delivery over the time period between 1500 CE and the present.

Sediment profiles of δ^{13} C document specific periods of positive excursion, consistent with increasing primary production over time (Fig. 9). Values of δ^{13} C ranged from 23 to 22 per mil at the base of the cores (pre-1800) (Zimmerman and Canuel 2002). Between 1800 and 1900 CE, δ^{13} C values were variable (23 to 21.5 per mil) in the RD and RR cores, but remained constant (21.5 to 20 per mil) in the M3 core. Beginning in the early twentieth century, δ^{13} C values increased continuously to the most positive values (approximately 20 per mil), consistent with increasing phytoplankton production due to anthropogenic nutrient inputs. Consistent with this interpretation, δ^{13} C values were correlated with organic carbon-normalized concentrations of plankton biomarkers in the cores (r=0.70–0.95; p<0.001).

Similarly, positive excursions in the $\delta^{15}N$ profiles in these three cores document changes in the Bay's ecology over time, but there was more between-core variability in the timing of the ${}^{15}N$ enrichments (Fig. 9). At RD, the most northerly site, $\delta^{15}N$



Fig. 9 Stable isotope profiles in three sediment cores collected from the mesohaline region of Chesapeake Bay. Reprinted with permission by the American Society of Limnology and Oceanography. Copyright (2002) by the American Society of Limnology and Oceanography, Inc.

signatures increased almost continuously from approximately 5 per mil in 1700 CE to 8.5 per mil in 2000 CE, with the steepest rate of change between the 1940s and 1970s. Organic matter in sediments, collected from an intermediate depth at site M3, contained the same 5 per mil signature in the lower portion of the core, but here, the positive trend in δ^{15} N values begins in the early nineteenth century and values are high (approximately 7 per mil) and variable in sediments deposited between 1900 and 2000 CE. In the shallowest core location, RR, δ^{15} N values do not increase until around 1900 CE. The timing of these δ^{15} N signatures are synchronous

with total organic carbon deposition and most likely represent increasing microbial processing (e.g., nitrification and denitrification) of increasing amounts of OM reaching the sediment due to eutrophication-driven water column anoxia. As eutrophication and anoxia strengthen, the effects move higher in the water column (i.e., from site RD to M3 to RR). Thus, ¹⁵N seems to represent an isotopic marker for anoxia, in this case.

In a subsequent study, stable carbon and nitrogen isotopes were used to examine anthropogenic and climate effects on the Chesapeake Bay ecosystem over the past 2700 years (Bratton et al. 2003b). Some of the sites sampled for this work overlapped with those studied by Zimmerman and Canuel (2002), both corroborating and extending the δ^{13} C and δ^{15} N records to longer timescales. For example, in this study, sediment core profiles of δ^{13} C were explained as changes in the proportion of terrestrial organic matter delivered to the estuary, reflecting oscillations in river discharge. Wet periods, characterized by lower δ^{13} C values, were identified around 1935, 1800, 1560 CE, and 970 and 300 before CE (BCE).

In another study, negative $\delta^{13}C$ excursions were correlated to relatively wetter periods, which, because of their inverse correlation with sedimentary organic carbon to nitrogen ratios, were attributed to higher primary productivity associated with greater runoff nutrient delivery (Mitra et al. 2009). The past millennia was found to be wetter, overall, than the previous one, and characterized by higher frequency wet/dry oscillations. Both of these changes may be associated with longterm shifts in the strength of North Atlantic thermohaline circulation.

 δ^{15}

M3), and a subsequent increase of 1.5-fold between 1880 and 1950. However, TOC accumulation rates remained constant in the surface of the cores, which represented accumulation since the 1980s.

Organic biomarkers were used to investigate whether there were changes in the OM composition over the timeframe represented by the cores. Using a combination of lipid biomarkers, representing potential sources of OM (see Table 4), and accounting for the losses that can be calculated to have occurred due to decomposition, Zimmerman and Canuel (2002) documented that algal and bacterial sources increased 1.5 to 2-fold during the nineteenth century and as much as 2- to 6-fold during the twentieth century (Fig. 10). In comparison, biomarkers for terrigenous sources increased more slowly (1.5- to 3-fold) during the twentieth century. These data show that the mesohaline region of Chesapeake Bay has become enriched in microbial and algal sources of organic matter over this time period. Mechanisms driving these enrichments were investigated and the authors found positive correlations between plankton and bacterial biomarkers and human population in the watershed ($r^2 = 0.70$ and 0.81; p < 0.01, respectively). The data also showed positive relationships with fertilizer use in the watershed ($r^2 = 0.60$ and 0.46; p < 0.01, respectively). In contrast, biomarkers for terrigenous sources of organic matter were inversely related to population ($r^2 = 0.82$; p < 0.01) and had no relationship to fertilizer use in the Chesapeake Bay watershed. Together, organic proxies document changes in carbon delivery, as well as increased contributions from algal and bacterial production, with the greatest enrichments occurring since the 1950s.



Fig. 10 Sediment core profiles showing enrichment factors for algal, bacterial and terrestrial organic matter calculated from organic biomarkers. Reprinted with permission by the American Society of Limnology and Oceanography. Copyright (2002) by the American Society of Limnology and Oceanography, Inc.

Enrichment Factor

Other classes of organic compounds, polycyclic aromatic hydrocarbons (PAH) and black carbon (BC), have been used to document changes in the delivery of carbon sources to the Bay due to climatic variation within the Bay's water- and air-shed at longer time scales. Black carbon, the highly refractory residues from the combustion of plant biomass, was analyzed in a central Bay core via a series of demineralization and oxidation procedures (Mitra et al. 2009). These authors found that the ratio of BC to non-BC organic carbon increased during four centennial-scale dry periods over the past millennia, beginning with the late Medieval Warm Period, around 1100 CE. Further, the PAH and δ^{13} C signatures of this material indicated that it varied in both source distance and parent plant type. Isotopic enrichments in BC during dry periods are consistent with increased proportions of C4 grasses in the BC fraction and may be attributed to the competitive advantage of C4 plants during arid climatic periods or, perhaps, to their tendency to create exportable carbon when burned. These studies provide examples of how multiple biomarker proxies can provide information about the delivery of carbon to estuarine environments. We note that organic proxies provide useful tools for assessing the role of climate and anthropogenic activities on the carbon cycle in cases where fossils (i.e., hardparts) are not well preserved.

6 Summary and Considerations

While Chesapeake Bay is a relatively well-studied system, water quality monitoring efforts have been limited to the past several decades and are unable to provide information about pre-anthropogenic conditions. Historical data sets and sediment core records of fossil and chemical constituents provide alternative and complementary archives of information that are useful for extending our knowledge of the Bay beyond the timescale of these monitoring efforts (Kemp and Goldman 2008; Willard and Cronin 2007). An additional benefit is that proxies sequestered in contemporary organisms, and newly deposited sediments, can be calibrated to present environmental conditions to provide comparisons with pre-anthropogenic conditions in the Bay that can be useful for setting management and restoration goals.

Paleoecological approaches also provide useful information about the range of climate conditions the Bay has experienced over its history and how biological and physical variables have responded to these changing conditions. Temporal variations in climate result both from regional processes as well as global-scale forcings such as El Niño-Southern Oscillation, the Pacific Decadal Oscillation and the North Atlantic Oscillation. The International Panel on Climate Change recently concluded that human activities have contributed to climate change and projected further human-induced climate change in future decades (IPCC 2014). Climate change models for the mid-Atlantic predict that the Chesapeake Bay region will experience increases in CO_2 concentrations, sea level, water temperature, and the amounts and intensity of precipitation (Najjar et al. 2010

- Brush GS (1986) Geology and paleoecology of Chesapeake Bay: a long-term monitoring tool for management. J Wash Acad Sci 76:146–160
- Brush GS (1989) Rates and patterns of estuarine sediment accumulation. Limnol Oceanogr 34:1235–1246
- Brush GS (2001a) Forests before and after the colonial encounter. In: Curtin PD, Brush GS, Fisher GW (eds) Discovering the Chesapeake. Johns Hopkins University Press, Baltimore
- Brush GS (2001b) Natural and anthropogenic changes in Chesapeake Bay during the last 1000 years. Hum Ecol Risk Assess 7:1283–1296
- Brush GS (2009) Historical land use, nitrogen, and coastal eutrophication: a paleoecological perspective. Estuaries Coasts 32:18–28
- Brush GS, Brush LM (1994) Transport and deposition of pollen in an estuary: a signature of the landscape. In: Traverse A (ed) Sedimentation of organic particles. Cambridge University Press, Cambridge
- Brush GS, DeFries RS (1981) Spatial distributions of pollen in surface sediments of the Potomac estuary. Limnol Oceanogr 26:295–309
- Brush GS, Hilgartner WB (2000) Paleoecology of submerged macrophytes in the upper Chesapeake Bay. Ecol Monogr 70:645–667
- Canuel EA, Martens CS (1996) Reactivity of recently deposited organic matter: degradation of lipid compounds near the sediment-water interface. Geochim Cosmochim Acta 60:1793–1806
- Canuel EA, Cloern JE, Ringelberg DB et al (1995) Using molecular and isotopic tracers to examine sources of organic matter and its incorporation into the food webs of San Francisco Bay. Limnol Oceanogr 40:67–81
- Carroll M, Kowalewski M, Simoes MG et al (2003) Quantitative estimates of time-averaging in terebratulid brachiopod shell accumulations from a modern tropical shelf. Paleobiology 29:381–402
- Cloern JE (2001) Our evolving conceptual model of the coastal eutrophication problem. Mar Ecol Prog Ser 210:223–253
- Cloern JE, Canuel EA, Harris D (2002) Stable carbon and nitrogen isotope composition of aquatic and terrestrial plants of the San Francisco Bay estuarine system. Limnol Oceanogr 47:713–729
- Colman SM, Bratton JF (2003) Anthropogenically induced changes in sediment and biogenic silica fluxes in Chesapeake Bay. Geology 31:71–74
- Colman S, Mixon R (1988) The record of major quaternary sea-level changes in a large coastal plain estuary, Chesapeake Bay, Eastern United States. Paleogeogr Paleoclimatol Paleoecol 68:99–116
- Cooper SR (1995) Chesapeake Bay watershed historical land use: impact on water quality and diatom communities. Ecol Appl 5:703–723
- Cooper SR, Brush GS (1991) Long-term history of Chesapeake Bay anoxia. Science 254:992–996
- Cornwell JC, Conley DJ, Owens M et al (1996) A sediment chronology of the eutrophication of Chesapeake Bay. Estuaries 19:488–499
- Cronin TM (2000) Initial Report on IMAGES V Cruise of Marion-Dufresne to Chesapeake Bay June, 1999. U.S. Geological Survey Open-file Report 00-306
- Cronin T, Ishman S (2000) Holocene paleoclimate from Chesapeake Bay ostracodes and benthic foraminifera from Marion-Dufresne core MD99-2209. In: Cronin T (ed) Initial report of IMAGES V cruise of the Marion-Dufresne to the Chesapeake Bay June 20-22, Vol 00-306, U.S. Geological Survey
- Cronin TM, Vann CD (2003) The sedimentary record of anthropogenic and climatic influence on the Patuxent Estuary and Chesapeake Bay ecosystems. Estuaries 26:196–209
- Cronin TM, Walker H (2006) Restoring coastal ecosystems and abrupt climate change. Clim Chang 74:369–374
- Cronin TM, Willard DA, Kerhin RT et al (2000) Climatic variability over the last millennium from the Chesapeake Bay sedimentary record. Geology 28:3–6
- Cronin TM, Dwyer GS, Kamiya T et al (2003a) Medieval warm period, little ice age and 20th century temperature variability from Chesapeake Bay. Global Planet Change 36:17–29

Cronin TM, Sanford L, Langland M et al (2003b) Estuarine sediment transport, deposition, and sedimentation. In: Langland M, Cronin T (eds) U.S. Geological Survey Water-Resources Investigations Report 03-41

Cronin TM, Thunell R, Dwyer GS et al (2005) Multiproxy evidence of Holocene climate variabil-

- Kemp WM, Goldman EB (2008) Thresholds in the recovery of eutrophic coastal systems. Maryland Sea Grant, College Park, MD
- Kemp WM, Boynton WR, Adolf JE et al (2005) Eutrophication of Chesapeake Bay: historical trends and ecological interactions. Mar Ecol Prog Ser 303:1–29
- Kidwell SM (2001) Preservation of species abundance in marine death assemblages. Science 294:1091–1094
- Kidwell SM, Bosence DWJ (1991) Taphonomy and time-averaging of marine shelly faunas. In: Allison PA, Briggs DEG (eds) Taphonomy. Plenum Press, New York
- Kidwell SM, Best MMR, Kaufman DS (2005) Taphonomic trade-offs in tropical marine death assemblages: differential time averaging, shell loss, and probable bias in siliciclastic vs. carbonate facies. Geology 33:729–732
- Killops SD, Killops VJ (1993) Chemical composition of biogenic matter. In: An introduction to organic geochemistry. Wiley, New York

Kolbe SE, Morgan EE, Lockw death

- Saenger C, Cronin TM, Thunell R et al (2006) Modeling river discharge and precipitation from estuarine salinity in the northern Chesapeake Bay: application to Holocene paleoclimate. The Holocene 16:1–11
- Saenger C, Cronin TM, Willard D (2008) Increased terrestrial to ocean sediment fluxes in the northern Chesapeake Bay with twentieth century land alteration. Estuaries Coasts 31:492–500
- Stevenson JC, Marusic JI, Ozreetic B et al (1999) Shallow water and shore line ecosystems of the Chesapeake Bay compared to the northern Adriatic Sea: transformation of habitat at the landsea margin. In: Malone T, Malej A, Harding LW Jr, Smodlaka N, Turner RE (eds) Ecosystems at the land-sea margin: drainage basin to coastal sea. American Geophysical Union, Washington, DC, pp 29–76
- Summons RE, Jahnke LL, Hope JM et al (1999) 2-Methylhopanoids a biomarkers for cyanobacterial oxygenic photosynthesis. Nature 400:554–557
- Sun M-Y, Wakeham SG (1994) Molecular evidence for degradation and preservation of organic matter in the anoxic Black Sea basin. Geochim Cosmochim Acta 58:3395–3406
- Sun M-Y, Wakeham SG, Lee C (1997) Rates and mechanisms of fatty acid degradation in oxic and anoxic coastal marine sediments of Long Island Sound, New York, USA. Geochim Cosmochim Acta 61:341–355
- Vaalgamaa S, Sonninen E, Korhola A et al (2013) Identifying recent sources of organic matter enrichment and eutrophication trends at coastal sites using stable nitrogen and carbon isotope ratios in sediment cores. J Paleolimnol 50:191–206
- Volkman JK, Smittenberg RH (2017) Lipid biomarkers as organic geochemical proxies for the paleoenvironmental reconstruction of estuarine environments. In: Weckström K, Saunders KM, Gell PA, Skilbeck CG (eds) Applications of paleoenvironmental techniques in estuarine studies, vol 20, Developments in paleoenvironmental research. Springer, Dordrecht
- Wakeham SG, Canuel EA (2006) Degradation and preservation of organic matter in marine sediments. In: Volkman J (ed) Marine organic matter: biomarkers, isotopes and DNA, vol 2, Handbook of environmental chemistry. Springer, Berlin
- Webb T (1993) Constructing the past from late Quaternary pollen data: temporal resolution and a zoom lens space-time perspective. In: Kidwell S, Behrensmeyer AK (eds) Taphonomic approaches to time resolution in taphonomic assemblages, vol 6. Paleontological Society, Knoxville
- Wehmiller J, Miller G (2000) Aminostratigraphic dating methods in Quaternary geology. In: Noller J, Sowers J, Lettis W (eds) Quaternary geochronology: methods and applications, 4th edn. American Geophysical Union, Washington, DC
- Willard DW, Cronin TM (2007) Paleoecology and ecosystem restoration: case studies from Chesapeake Bay and the Florida Everglades. Front Ecol Environ 5:491–498
- Willard DA, Korejwo DA (2000) Holocene palynology from Marion-Dufresne cores MD99-2209 and 2207 from Chesapeake Bay: impacts of climate and historic land-use change. In: Cronin T (ed) Initial report on IMAGES V cruise of the Marion- Dufresne to the Chesapeake Bay June 20-22, 1999
- Willard DA, Cronin TM, Verardo S (2003) Late-Holocene climate and history from Chesapeake Bay sediment cores, USA. The Holocene 13:201–214
- Yuan S (1995) Postglacial history of vegetation and river channel geomorphology in a Coastal Plain floodplain. Ph.D. Dissertation, Johns Hopkins University, Baltimore, MD
- Zimmerman AR, Canuel EA (2000) A geochemical record of eutrophication and anoxia in Chesapeake Bay sediments: Anthropogenic influence on organic matter composition. Mar Chem 69:117–137
- Zimmerman AR, Canuel EA (2001) Bulk organic matter and lipid biomarker composition of