

Chapter 20

Paleoecology Studies in Chesapeake Bay: A Model System for Understanding Interactions Between Climate, Anthropogenic Activities and the Environment

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Abstract Sediments provide one of the best reservoirs of information of how aquatic ecosystems have been altered by natural (climate change) and human agents over time. This information is preserved in a variety of biogenic materials including macro- and microfossils, pollen and chemical proxies, which record ecological responses to past perturbations. Chesapeake Bay, the largest estuary in the United States, is particularly well-suited to paleoenvironmental studies due to high rates of sediment accumulation, good preservation potential and historical records that can be used to corroborate evidence of change over the past several centuries. Previous paleoecological studies in Chesapeake Bay have examined how climate change and human activities have modified vegetation, species composition, sediment supply and carbon delivery over time. In this chapter, we review a variety of paleoecological approaches that have been employed to understand how the Bay ecosystem has changed over time. These proxies include

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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 kiloyear (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 development. For example, at about 15 ka, during the last deglaciation, climatic warming caused major floral changes in the terrestrial ecosystems around the Bay characterized by a shift from primarily conifers to a mix of coniferous and angiospermous species, such as oak, maple and hickory (Yuan 1995). Near the end of deglaciation, global sea level rise reached the mouth of the Bay, drowning the Susquehanna paleochannel between 9 and 7 ka (Bratton et al. 2003a; Cronin et al. 2007). As the rate of sea level rise decreased, freshwater wetlands and coastal salt marshes expanded. The Bay assumed its current configuration over the last 6 ka as the global sea level rise ceased but the mid-Atlantic region continued to undergo regional subsidence and relative sea level rise of about 1 mm year⁻¹ caused by glacio-isostatic adjustment.

In addition to its evolving climate and landscape, the Chesapeake Bay region has been profoundly influenced by human activities in its watershed beginning with the arrival of the first humans, possibly as early as 10,000 years ago (Fig. 2) (Rountree 1996). As human populations increased, first by native Americans, and then by European colonists, land was cleared for hunting, agriculture and fishing, which altered the aquatic ecosystem (Brush 2001a). By the 1700s, the first signs of environmental degradation were evident in Chesapeake Bay (<http://www.chesapeake-bay.net>). By the mid-1700s, 20–30% of the forests had been cleared causing the Bay's shipping ports to fill with eroded sediments (Gottschalk 1945). Even more dramatic changes to the Bay and its watershed began during the 1900s. Chemical

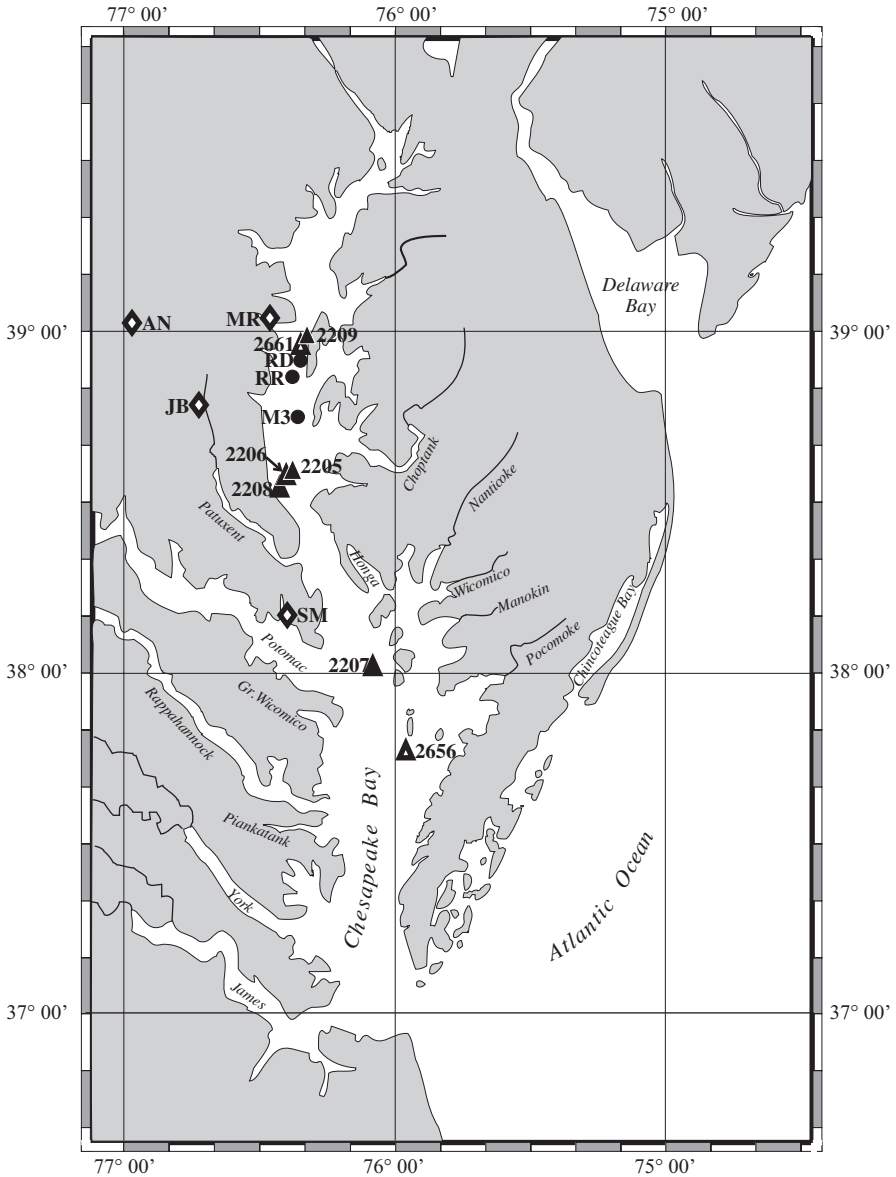


Fig. 1 Map showing Chesapeake Bay and locations of studies described in this chapter. The symbols refer to the different types of studies (i.e., pollen studies (*open diamonds* showing locations for MR Magothy River, JB Jug Bay, SM St. Mary's, AN Anacostia), biomarker studies (*filled circles* for core locations RD, M3 and RR), benthic mollusk studies (*open triangles* with USGS core numbers 2661 (Kent Island) and 2656 (Pocomoke River)), and microfossil cores (*filled triangles* with USGS core numbers))

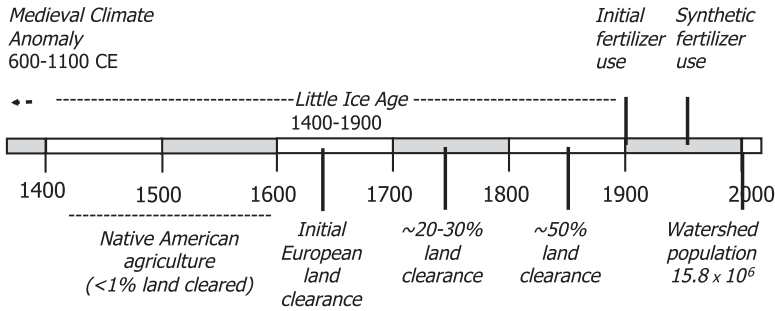


Fig. 2 Timeline with examples of climate and land use changes in Chesapeake Bay and its watershed

fertilizers were first introduced following World War I but their use was interrupted during World War II (Stevenson et al. 1999). In 1945, application of chemical fertilizers resumed and subsequently expanded. Fertilizer use, as well as runoff from livestock operations, has continued to expand into the present, resulting in the delivery of excess nutrients and declining water quality. The Bay watershed has also been dramatically changed since the 1950s in response to increasing human populations, land-use shifts and increased urbanization. A major perturbation to the Bay ecosystem occurred during the late 1970s when submerged aquatic vegetation was reduced dramatically (Brush and Hilgartner 2000). By 2000, when the population in the Bay watershed reached 15.8 million, the distribution of submerged grasses had been further reduced, eutrophication and summertime hypoxia were extensive, and fish stocks were depleted (<http://www.chesapeakebay.net/>).

Changes to the Chesapeake Bay watershed have influenced the amount, form and composition of a wide variety of substances (e.g., sediments, contaminants, inorganic nutrients and organic matter) delivered to this estuary. In recent decades, these changes have contributed to deteriorating water quality, reductions in wetland and seagrass habitat, and altered ecosystem services (Kemp et al. 2005). Many of these environmental problems are similar to those impacting estuaries on a global basis (Cloern 2001; Lotze et al. 2006).

In this chapter, we review a variety of approaches that have been employed for understanding how the Bay ecosystem has changed over time, in response to both climate and human perturbations. A common thread in these studies is the use of a wide variety of proxies (chemical fingerprints, microscopic remains and fossils) preserved in sediment core records (Brush 1986; Cooper and Brush 1991; Cooper 1995; Brush and Hilgartner 2000; Cornwell et al. 1996; Zimmerman and Canuel 2000, 2002; Willard and Cronin 2007). One of the key benefits of this approach is that it allows for the evaluation of changes to Chesapeake Bay that pre-date even the longest and most well-established monitoring efforts. Sediment cores also provide the ability to examine the influence of both long time-scale climatic variations as well as changes occurring over historical timescales. While Chesapeake Bay is well-suited for the application of this approach, due to its high sediment accumulation

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.

2.1 *Methods for Pollen Studies*

The majority of sediment cores used for pollen studies were collected using a hand-operated 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 1984). Dates for agricultural horizons are obtained from the U.S. Agricultural Census published since 1840 and earlier historical records (Table 1). The historical and radiocarbon dates provide average pre-European and post-European sedimentation rates (Table 1).

Sedimentation rates for individual layers of a core, necessary for calculating the influxes, are estimated by adjusting the average sedimentation rates between dated horizons (based on pollen and carbon-14 dates) according to the total pollen concentration in each individual layer using the following equation (Brush 1989);

Table 1 Pollen horizons used to date sediment cores

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 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

$$R_{0.1} = (n / n_{0.1})R, \text{ where}$$

$R = d/t =$ 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).

2.2 *Vegetation History of Chesapeake Bay Watershed: The Interaction of Geology, Soils and Climate*

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).

The Anacostia site (39°01' N, 76°54' W), on a tributary of the Potomac River close to Washington, DC, is the most mesic location with clay and loam soils supporting a tulip, poplar and river birch forest (Fig. 1). The St. Mary's site (38°011' N, 76°26' W), located at the lower Potomac, is characterized by willow oak and loblolly pine growing on a somewhat drier clay and sandy loam. The Magothy River site (39°05' N, 76°29' W) consists of "dry" oak species occurring on a sand and fragipan substrate, with a low water holding capacity. Ragweed dominates the pollen profiles at all three sites since the time of European colonization, approximately 350 years ago (Table 3). Prior to European colonization, changes in the pollen profiles reflect a response to climate change, and though synchronous, differ from one site to another depending on the soil substrate. Thus the flora at the Anacostia site changed from hemlock and pine to oak and ericaceous plants at about 6 ka. At the same time, the St. Mary's forests changed from possibly hemlock to Cupressaceae (red cedar, Atlantic white cedar, and/or bald cypress) and, later, to alder, maple and oak with sphagnum moss. At the Magothy site, sweet gum and black gum dominate the pollen profiles after 5 ka and were followed by oak and pine at about 3 ka.

Table 3 Summary of spatial-temporal changes in three cores collected from the Chesapeake Bay region as determined by pollen composition

	Anacostia site	St. Mary's site	Magothy site
Modern Forest	Tulip poplar, river birch, sycamore	Willow oak and loblolly pine	Tulip poplar, post oak, blackjack oak and chestnut oak
Substrate	Clay and loam	Clay and sandy loam	Sand and fragipan
350 y BP	Agricultural ragweed	Agricultural ragweed	Agricultural ragweed
2.5 ka	Ericaceae, oak and charcoal	Sphagnum, alder, maple and oak	Oak and pine
4 ka			Sweet gum and black gum
6 ka		Cupressaceae	
9 ka	Hemlock and pine	Hemlock (maybe)	
12 ka	Birch, decrease in pine		
14 ka	Fir, pine and spruce		

Site locations are provided in Fig. 1

2.3 *Vegetation History of the Chesapeake Bay Watershed: Two Examples*

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). The Anacostia example, referred to above, is characterized by low sedimentation rates and hence low resolution. In this core, vegetation response to long-term climate change throughout the Holocene is shown (Fig. 3) (Brush 2001b). In comparison, the Jug Bay example (38°46' N, 76°41' W) is from a fresh tidal wetland in the upper Patuxent River (Fig. 4). It has higher sedimentation rates and higher resolution, and, therefore, spans a much shorter period of time. The higher resolution allows shorter climatic intervals to be recorded, such as the Medieval Warm Period (MWP), which occurred about 600–1100 Common Era (CE) (Brush 2001b). Together, these records provide examples of the application of fossil pollen/seed records to different timescales of environmental change.

The Anacostia core (i.e., Dan's Bog Core), about 1.5 m in length, spans 14 ka and almost the entire Holocene (Fig. 3). The chronology in this core was derived, as described above, from average sedimentation rates between three carbon-14 dates and the agricultural ragweed horizon. From 14 to about 11 ka, pollen of fir (*Abies*) and spruce (*Picea*) occur along with pine, some oak (*Quercus*), a lot of alder (*Alnus*) and paper birch (*Betula*) (identified from seeds). There is an abundance of sedges (Cyperaceae), as well as composites (Asteraceae) and grasses (Poaceae). The Younger Dryas (a cooler period) is represented in the core by an increase in spruce and pine followed by a decrease in both taxa between 13 and 12 ka. This period is followed by a loss of spruce and fir, an increase in pine, and the introduction of hemlock between 10 and 6 ka. During this time period, oak increases, alder decreases, and birch is greatly reduced. Sedges are greatly reduced and the grasses disappear. Small amounts of pollen of the blueberry family (*Ericaceae*) emerge at this time. After 6 ka B.P., pine decreases, oak increases and members of the blueberry family, including arrowwood (*Viburnum*), become abundant at 3.5 ka ago. In summary, the vegetation history shows a change from early Holocene boreal conditions to a period, from 10 to 6 ka, when temperatures ameliorated but conditions were wetter than at present and there was not much understory. There is an abundance of charcoal in the sediments around 6 ka (not shown in Fig. 3) at which time the modern mesic to dry forest emerged. The period of colonization is marked by a large increase in ragweed (*Ambrosia*).

The core collected from Jug Bay spans 1.5 ka (Fig. 4) and shows changes in trees and wetland taxa during the Medieval Warm Period. During that time, pollen of walnut (*Juglans*), a tree which grows in wet habitats, decreased dramatically while pollen of dry taxa, such as oak and holly (*Ilex*), increased. Similarly, there are large decreases in seeds of wetland plants such as wild rice (*Zizania*) and pickerelweed (*Pontederia*). An initial increase in ragweed is followed by a large increase during colonization. The increase in ragweed is accompanied by an increase in pollen of the high marsh arrowhead (*Sagittaria*), suggesting drier conditions probably due to sediment infilling of the marsh.

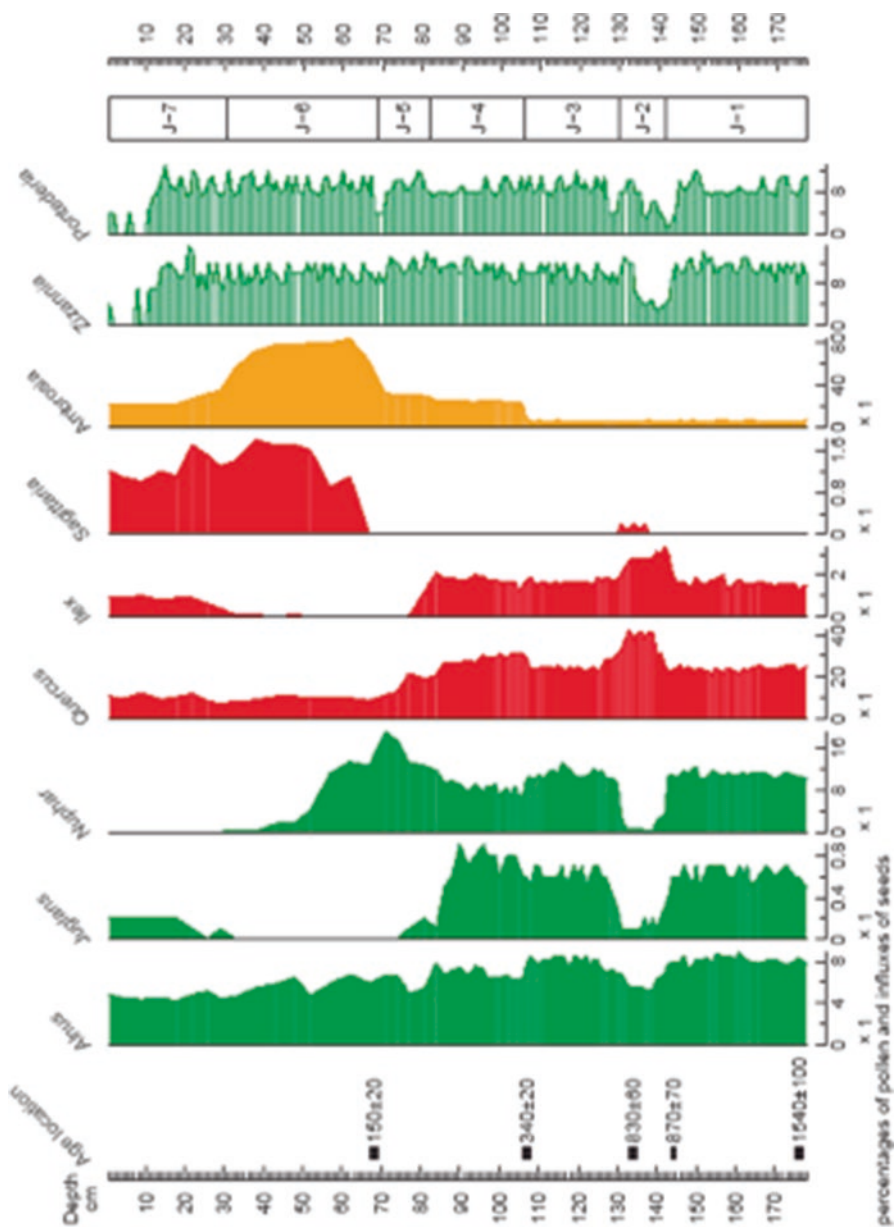


Fig. 3 Downcore profile of pollen isolated from the Anacostia River, located near Washington DC, showing how vegetation changed in response to climate change throughout the Holocene (Yuan 1995)

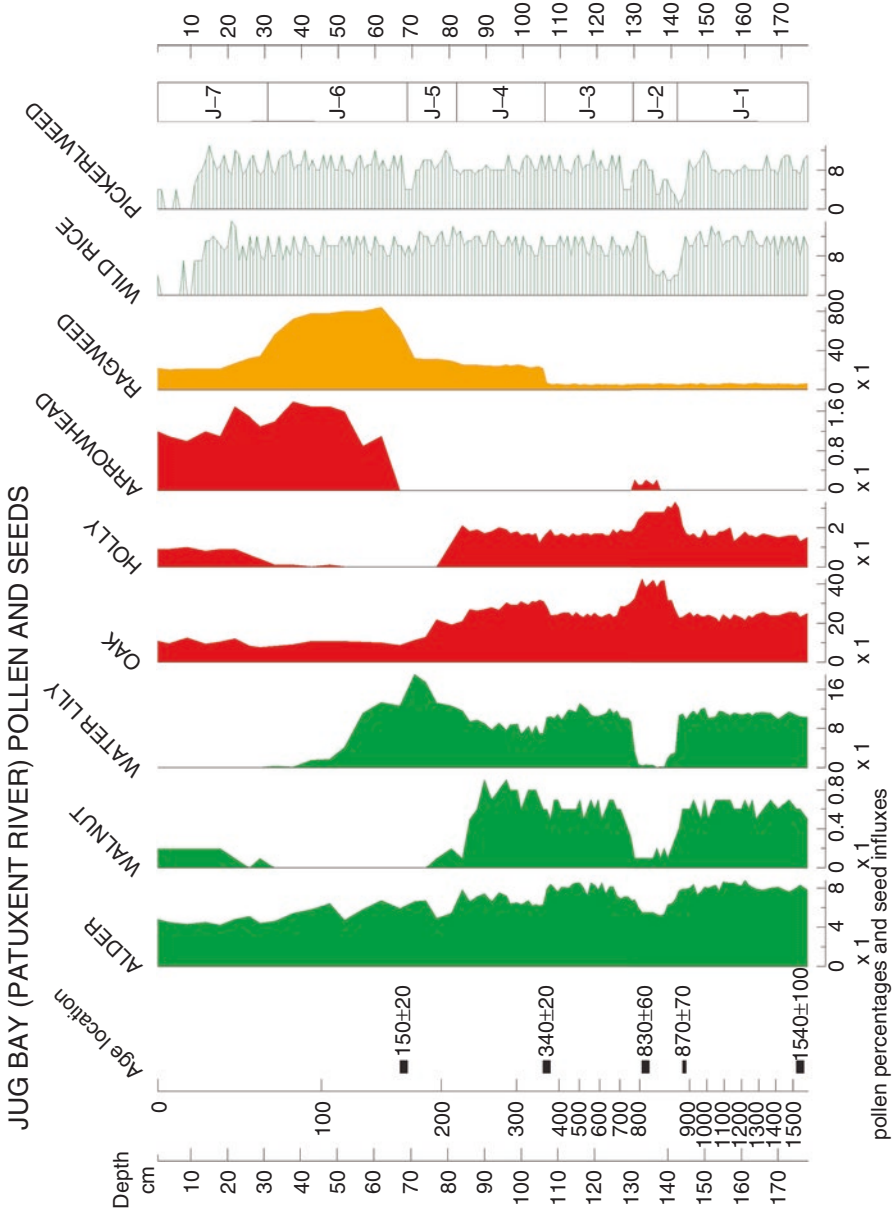


Fig. 4 Downcore profile of pollen isolated from Jug Bay located on the Patuxent River, Maryland showing changes in vegetation since the Medieval Warm Period (1000 years before present (BP))

As stated previously, the level of detail with which changes in vegetation can be retrieved from sediment cores is limited by the temporal resolution, which is determined by sedimentation rates. Sedimentation rates can differ significantly from one location to another, even when sites are in close proximity to one another. The sediment cores also document the change from a pre-Colonial, heterogeneous forested landscape to a more homogeneous, non-forested landscape dominated by ragweed and other herbaceous plants, following European colonization.

3 Calcareous Microfossils

Two calcareous microfossil groups have been used to study estuarine ecosystem and climatic history in Chesapeake Bay: benthic foraminifera (protists) and ostracods (benthic Crustacea). Foraminifers and ostracods are important components of the Bay's meiofauna and readily fossilize in its sediments. Research has emphasized temporal patterns in individual species, faunal assemblages, and chemistry of their calcareous (CaCO_3) shells obtained from radiometrically dated sediment cores collected on multi-disciplinary cruises (e.g., Cronin 2000). Studies of foraminifers and ostracods carried out in conjunction with other proxies, such as pollen, dinoflagellates and sediment geochemistry, have provided the most robust paleo-reconstructions of estuarine environmental changes caused by human activity and natural climate variability (e.g. Willard et al. 2003; Willard and Cronin 2007). We summarize here three specific applications of calcareous microfossils to the paleoenvironmental history of Chesapeake Bay.

3.1 *Climate Variability and Ecosystem Functioning*

Climate change is recognized as a major forcing factor in estuarine functioning throughout North America (Cronin and Walker 2006). Climate variability over inter-annual to centennial timescales poses unique challenges for ecosystem management because instrumental records of temperature, salinity and other key parameters are too short to fully understand climate's impacts on river discharge, salinity, productivity and dissolved oxygen levels. In addition, despite the focus by climate and estuarine modelers on simulating future temperature and precipitation regimes altered by anthropogenic greenhouse gases, climate variability exerts a greater influence on bay ecosystems than long-term changes in mean conditions. It is also likely that mean regional temperature over the next century will be unlike that seen in the past few millennia, making studies of periods like the early Holocene "thermal maximum" especially important for estuarine science.

The major mode of climate variability affecting Chesapeake Bay is the North Atlantic Oscillation (NAO), although El Niño-Southern Oscillation (ENSO) and Pacific North American (PNA) oscillation also can be important. The NAO is pri-

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 *Elphidium* (Cronin et al. 2005; Saenger et al. 2006). Water temperature is reconstructed using magnesium/calcium (Mg/Ca) ratios in the ostracod *Loxococoncha* (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.

3.2 *Sea Level Change*

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 margin of the North American Laurentide Ice Sheet at the peak of the last glacial period, called the last glacial maximum (LGM) about 21 ka. At the LGM, regions under the ice sheet were isostatically depressed due to its weight. Conversely, the mid-Atlantic region was isostatically uplifted and this phenomenon is known as the peripheral bulge. Since deglaciation and ice sheet retreat starting about 20 ka,

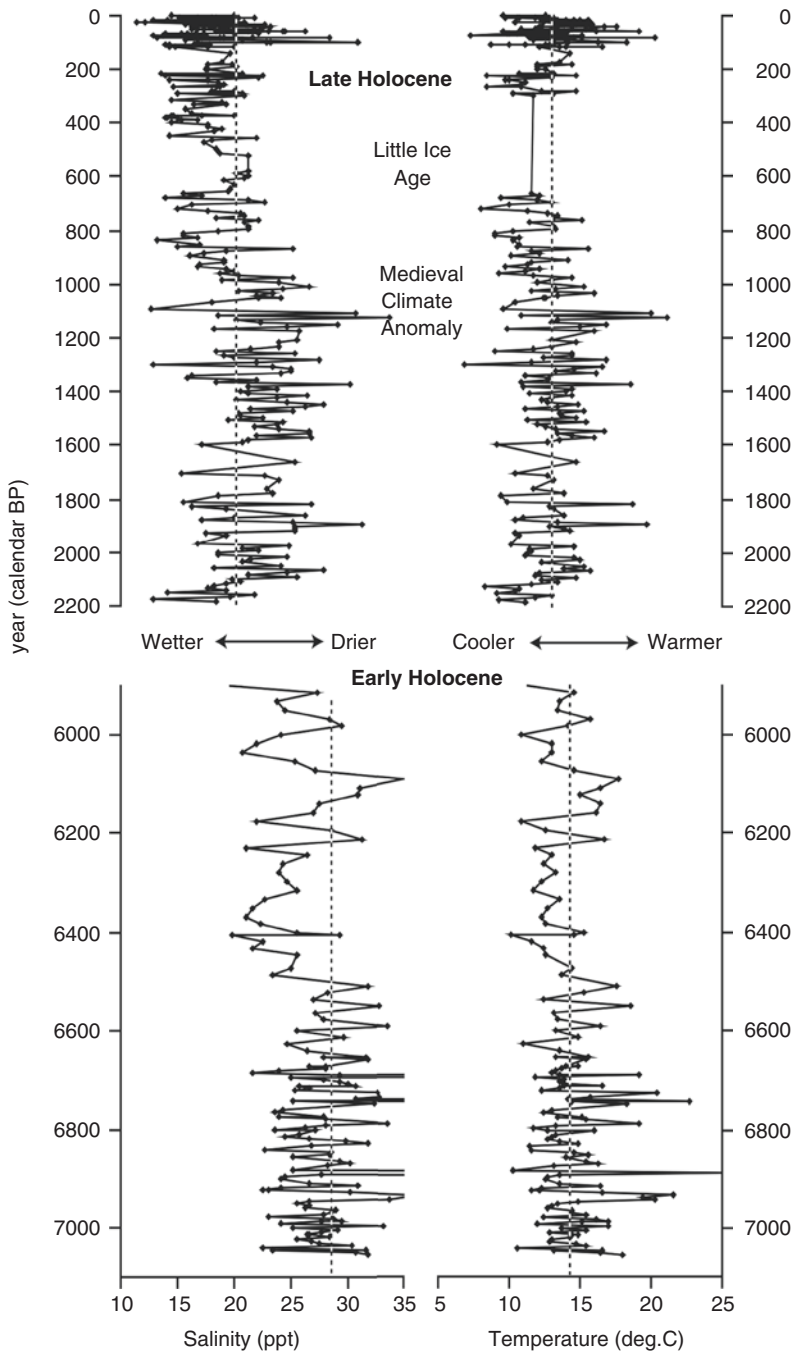


Fig. 5 Comparison of paleosalinity from foraminiferal oxygen and carbon isotopes and Mg/Ca-based paleotemperature records from Chesapeake Bay cores MD2209 and RD-98 modified from Cronin et al. (2003a, b, 2005). Figure shows drier and warmer early Holocene regional climate compared to conditions during 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 paleo-reconstructions provide definitive evidence that SLR during periods of rapid climatic warming has major ecological impacts on coastal marshes.

3.3 Water Quality: Dissolved Oxygen and Turbidity

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. Karlson 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

reduced levels of dissolved oxygen in estuaries. These indicator species are extremely rare in faunal assemblages obtained from sediment dated before colonial settlement, but increase gradually in the nineteenth century, and then rapidly during the second half of the twentieth century to become dominant components of the Bay's meiofauna. Their increased abundances are associated with colonial land-clearance and the massive increase in fertilizer use since the 1950s. Late twentieth century hypoxia was probably exacerbated by much wetter mean conditions since about 1970 when the NAO index returned to a positive mode. These changes, inferred from the benthic meiofauna, are supported by evidence from biogenic silica measured in bay sediment cores (Colman and Bratton 2003) and also diatoms (Cooper 1995).

Cronin et al. (2003b) and Saenger et al. (2008) conducted quantitative analyses of sediment flux from the Bay's watershed comparing pre- and post-colonial rates of sediment accumulation. They compared records from 15 sediment cores collected from the mainstem of the Bay with flux calculations from three regions in the greater Bay watershed system: watershed land surfaces to rivers and tributaries, fluvial sediments at river fall lines, and fluvial load to deposition in tributaries. They discovered that sediment flux increased by 138–269 % across all four regions after colonial land clearance and that sediment delivery exhibits a significant lag from surface erosion to final burial in the Bay. The evidence that some of the post-land clearance sediment loads are temporarily stored in the watershed en route to the Bay has important implications for land management decisions to reduce sediment influx and turbidity. Together, these studies provide examples of ways in which paleoecological proxies have been used successfully to provide information about past changes in water quality in Chesapeake Bay.

4 Benthic Mollusks

In contrast to the pollen and calcareous microfossil records highlighted above, the Holocene record of Chesapeake Bay mollusks has received considerably less attention until recently. Recent work has focused on the necessary first step in any paleoecological study—quantifying the extent to which the record is influenced by preservational processes. As the sedimentary record of estuaries is increasingly used to develop paleoenvironmental and paleoclimatic reconstructions and to provide baselines for ecological restoration (e.g., Cooper and Brush 1991; Jackson et al. 2001; Pandolfi et al. 2003; Brush 2009), the drawbacks of these records need to be explicitly assessed. Here, we summarize recent work outlining taphonomic (i.e., preservational) effects on the Holocene molluscan record of Chesapeake Bay and describe a preliminary study on the historical ecology of Chesapeake Bay mollusks. We emphasize not only the results of this work, but the techniques used to assess the quality of the estuarine paleorecord.

The sedimentary record is biased as a result of a myriad of taphonomic processes (for reviews see Kidwell and Bosence 1991; Martin 1999). Generally speaking,

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 10^4 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.

4.1 Preservational Bias in Chesapeake Bay Mollusks

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).

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 live-community 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).

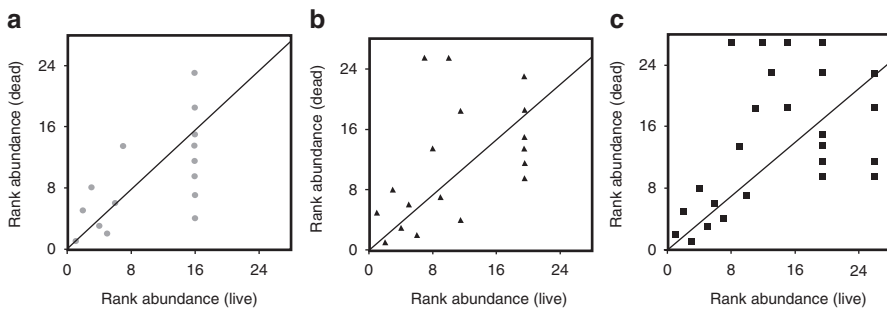


Fig. 6 Rank abundance of live benthic mollusks in the Chesapeake Bay is significantly correlated with rank abundance of mollusks in the death assemblage (Lockwood and Chastant 2006). This suggests that rank abundance of mollusks is faithfully recorded in the sedimentary record of the bay. Bivariate scatter 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 ($R_{24}=0.68$, $p=0.000$). (b) Data for 5 years of live sampling ($R_{26}=0.55$, $p=0.004$). (c) Data for 20 years of live sampling ($R_{29}=0.47$, $p=0.01$) (modified from Lockwood and Chastant (2006))

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.

4.2 Assessing Time Averaging in Chesapeake Bay Mollusks

Time averaging is defined as the mixing of non-contemporaneous fossil material such that specimens from successive generations, or ecologically unrelated communities, occur within a single sedimentary stratum (Fürsich and Aberhan 1990; Flessa et al. 1993). It can be quantified in a variety of ways, including (1) calculating maximum shell age (Kidwell et al. 2005), (2) age range (Flessa and Kowalewski 1994), (3) standard deviation (Kowalewski et al. 1998), and (4) shell half-life (Olszewski 1999)—all of which rely on some form of absolute dating. In recent years, amino acid racemization/epimerization (AAR) has become the preferred technique for quantifying time averaging in Quaternary-aged coastal and marine settings, in part because of its versatility, low cost, and applicability to a wide range of organisms and environments (Wehmiller and Miller 2000; Miller and Clarke 2007). The premise of this technique is that amino acids in living organisms, which are exclusively L-amino acids, will revert to equal proportions of D- and L- amino acids (racemic mixture) at a constant rate following the organism's death. Edwards (2007) was the first study to establish a radiocarbon-calibrated amino acid racemization (AAR) chronology for the Chesapeake Bay, and focused on time averaging within core-collected samples of the small opportunistic bivalve *Mulinia lateralis*.

Samples for the Edwards (2007) study were collected from two sediment cores, recovered via piston coring by the United States Geological Survey (USGS): (1) MD03-2661, drilled near Kent Island (38°53.21'N; 76° 23.89'W) in 25.5 m of water, reaching a core depth of 24.48 m, and recording a sedimentation rate ranging from 0.31 to 0.36 cm year⁻¹ and (2) MD03-2656, collected near the Pocomoke River (37°43.25'N; 75° 56.51'W) in 16.3 m of water, reaching a core depth of 16 m, and recording a sedimentation rate of approximately 0.2 cm year⁻¹ (Fig. 1). Full details of these cores are available at <http://geology>.

To create an age calibration curve for ¹⁴C and AAR, Edwards (2007) used both direct and indirect calibration methods after testing samples for internal consistency, or the coherent relationship between D/L aspartic acid (Asp) and D/L glutamic acid (Glu). For the direct calibration, radiocarbon ages and AAR analyses were obtained for eight articulated shells and for another eight shells that were bilaterally split. For the indirect calibration, radiocarbon age data from 11 core intervals were combined with AAR data for 178 *Mulinia* samples from the same

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).

Each shell was assigned an age based on direct calibration, then standard deviation and range of Asp-ages were calculated to estimate time averaging at each core depth. For the Kent Island core, time averaging in calendar years was assessed for 5–52 specimens per core depth, across 25 core depths for a total of 328 shells (Fig. 7). The two metrics yielded estimates of 720 years (standard deviation) and 2600 years (range) averaged across multiple depths in the Kent Island core. Time averaging increases with core depth, in part because of the manner in which the nonlinear nature of AAR racemization translates to the radiocarbon calibration. In general, time averaging (standard deviation) in the younger part of the Kent Island core

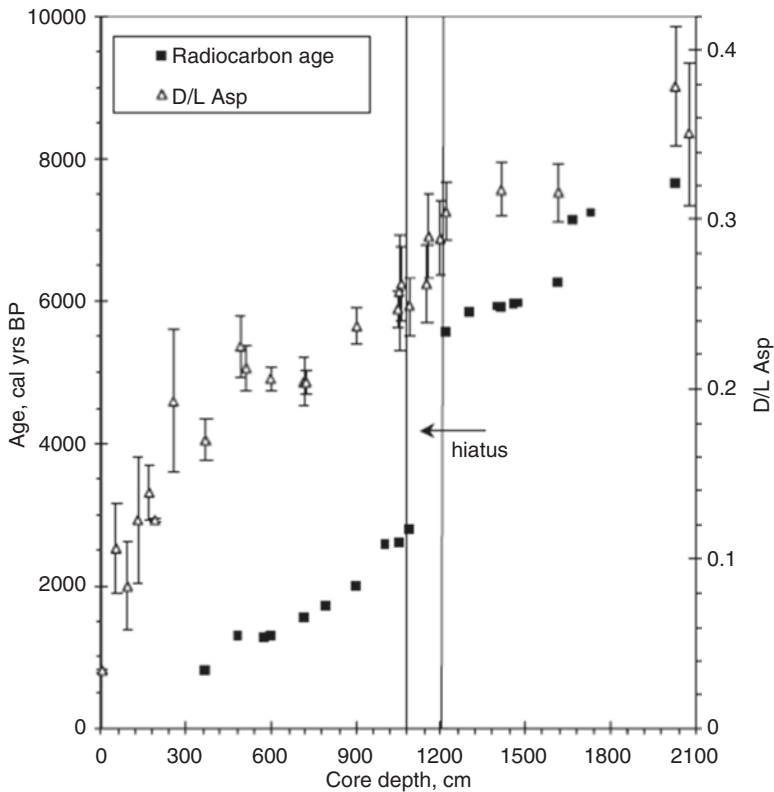


Fig. 7 Estimates for time averaging of benthic mollusks in the Chesapeake Bay range from centennial to millennial timescales, depending on the core depth examined and the time averaging metric used. Graph illustrates both the mean (\pm SD) AAR dates (*triangles*) and radiocarbon dates (*squares*) versus core depth, for samples of *Mulinia* bivalves from the Kent Island core (Edwards 2007). The condensed section (highlighted by vertical lines) is associated with a sudden increase in radiocarbon dates (modified from 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 ($\delta^{18}\text{O}$) in oyster shells at 0.3 mm intervals revealing extended drought conditions during the early years at the Jamestown settlement (1609–1616 CE) (Harding et al. 2010). This study developed a $\delta^{18}\text{O}$ calibration for modern oysters growing under a range of environmental conditions and compared $\delta^{18}\text{O}$ records from archaeological deposits with modern oysters.

Results presented in this chapter raise the obvious question of whether the fossils that are currently used for paleoenvironmental assessments and paleoclimate reconstruction, primarily foraminifera, pollen, and ostracods, record similar levels of preservational bias and time averaging. Unfortunately, few studies have tackled these questions for estuarine environments such as the Chesapeake Bay. A notable exception is Brush and DeFries (1981), which established that pollen accumulating in surface sediments along the Potomac River included most tree species and faithfully recorded the forest gradients adjacent to the river. Davis (1985) and Brush and Brush (1994) provide useful estimates of transport distances of a few meters for seeds and a few kilometers for tree pollen in the Chesapeake Bay region, respectively. Although these studies provide a useful baseline for pollen fidelity, we still need a much better picture of preservational bias in other fossil proxies, not to mention estimates of time averaging in both microfossils and plant material derived from Chesapeake Bay deposits.

4.3 *Exploring the Holocene Record of Benthic Mollusks in the Chesapeake Bay*

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., *Nucula proxima* (20–35 ppt), *Yoldia 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

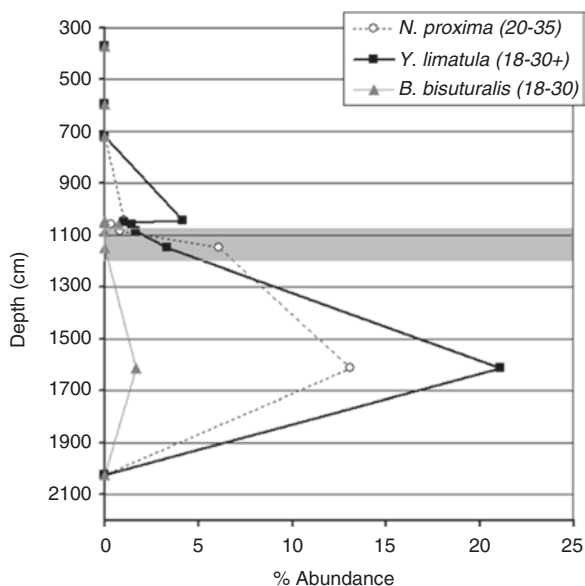


Fig. 8 Percent abundance of higher salinity molluscan species versus core depth in the Kent Island core. Higher salinity species, including *Nucula proxima*, *Yoldia limatula*, and *Boonea bisuturalis* (shown here with modern salinity tolerances) are statistically significantly higher in abundance in the early versus the late Holocene (modified from Kolbe et al. 2005). The boundary between the early and late Holocene (i.e., the condensed section in this core) occurs between 1088 and 1217 cm core depth (highlighted with the light grey box). The molluscan trends agree well with ostracod, foraminiferal, and pollen evidence for drier, warmer climatic conditions in the early Holocene

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.

5 Organic Proxies

5.1 Methods

Biomarkers are organic molecules that carry information about the sources of organic matter in a particular sample of water, soil, or sediment (Killops and Killops 1993; Volkman and Smittenberg 2017). Biomarker techniques have been applied successfully to biogeochemical studies tracing the sources of organic carbon in contemporary estuarine environments (Hedges and Keil 1999; Canuel et al. 1995; Zimmerman and Canuel 2001; Vaalgamaa et al. 2013) as well as to efforts

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 ($\delta^{13}\text{C}$ and $\delta^{15}\text{N}$) and lipid biomarker compounds.

Sediment records of the stable isotopes of carbon and nitrogen ($\delta^{13}\text{C}$ and $\delta^{15}\text{N}$) 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 ($\Delta^{14}\text{C}$) isotopes have been used as an additional tracer for organic matter sources (Raymond and Bauer 2001). The large range of potential $\Delta^{14}\text{C}$ values associated with organic matter delivered to estuarine environments increases the ability to resolve between sources in multi-isotope studies.

Lipid biomarker compounds provide an effective tool for tracing the sources of sedimentary organic matter in estuaries. Lipid biomarkers include a variety of structurally-diverse compounds for distinguishing between OM of vascular plant and soil (mostly terrigenous), algal (mostly aquatic) and petrogenic (fossil) origins (Table 4). While other classes of biomarkers provide unique tracers for terrigenous vascular plant sources (e.g., lignin phenols), lipids enable tracing of OM from both terrestrial and aquatic sources, as well as the effects of diagenesis through microbial activity. Although lipids are less affected by diagenesis than other biochemical classes, in reality, their reactivity spans a range from compounds that degrade on short time-scales (weeks to months) to compounds that persist in ancient sediments and petroleum (Freeman et al. 1990; Summons et al. 1999; Peters et al. 2005). Generally speaking, lipid stability increases with decreasing functionality, and information from field and laboratory studies of lipid reactivity can be used to select biomarkers appropriate for a given study (Sun and Wakeham 1994; Sun et al. 1997; Canuel and Martens 1996; Haddad et al. 1992). However, organic matter reactivity is not influenced by structure and functional group composition alone. Associations with inorganic and organic matrices, depositional conditions (e.g., oxygen exposure time) and a variety of other factors also influence the preservation of organic matter (Wakeham and Canuel 2006). By choosing lipid compounds that both represent the sources of OM of interest (e.g., algae, bacteria and vascular plants) and are stable at the time-scale of interest, organic biomarkers can be used to document changes in OM sources preserved in sediment cores (Zimmerman and Canuel 2000, 2002).

5.2 *Stable Isotope Studies in Chesapeake Bay*

In an effort to understand past changes in primary production and anoxia in Chesapeake Bay, Zimmerman and Canuel (2000, 2002) collected sediment cores from three sites (RD, M3 and RR) in the mesohaline region of Chesapeake Bay at

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)

	Compounds
<i>Fatty acid biomarkers</i> ^a	
Eubacteria	15:0, i15:0, a15:0, 16:1 ω 9, i17:0, a17:0, 17:0, 18:1 ω 7t, 18:1 ω 5, i19:0, a19:0
Sulfate-reducing bacteria	i17:1 ω 7, 10Me16:0, 17:1 ω 6
Aerobes	16:1 ω 7, 18:1 ω 7
Cyanobacteria	Same as eubacteria plus 18:2 ω 6
Diatoms	16:1 ω 3t, 20:5 ω 3
<i>Zostera marina</i> (seagrass)	18:1 ω 9, 18:1 ω 11, 18:3 ω 3, 26:0
Terrigenous to aquatic ratio	TAR _{FA} = $(n-C_{24} + n-C_{26} + n-C_{28}) / (n-C_{12} + n-C_{14} + n-C_{16})$
<i>Sterol biomarkers</i>	
Diatoms	24-methylcholest-5,22-dien-3 β -ol (brassicasterol) 24-methylcholesta-5, 24(28)-dien-3 β -ol
Fungi	24-methylcholest-5,7,22-trien-3 β -ol (ergosterol)
Crustaceans	cholest-5-en-3 β -ol (cholesterol)
<i>Zostera marina</i> (seagrass)	24-ethylcholest-5-en-3 β -ol (β -sitosterol) 24-ethylcholest-5,22-dien-3 β -ol (stigmasterol)
<i>n-Alkane biomarkers</i>	
Terrigenous to aquatic ratio	TAR _{HC} = $(n-C_{27} + n-C_{29} + n-C_{31}) / (n-C_{15} + n-C_{17} + n-C_{19})$

^aFatty acids are designated as follows: the number before the colon indicates the number of carbon atoms, the number after the colon indicates the number of carbon-carbon double bonds and the position of the initial unsaturation (double bonds) is indicated by the number of carbon units from the methyl, ω , end of the molecule. Fatty acids designated with “i” have a methyl group branch at the ω -1 position (iso-) and those designated with “a” have a methyl group branch at the ω -2 position (anteiso-)

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 ($\delta^{13}\text{C}$ and $\delta^{15}\text{N}$) were used to examine changes in C and N delivery over the time period between 1500 CE and the present.

Sediment profiles of $\delta^{13}\text{C}$ document specific periods of positive excursion, consistent with increasing primary production over time (Fig. 9). Values of $\delta^{13}\text{C}$ ranged from -23 to -22 per mil at the base of the cores (pre-1800) (Zimmerman and Canuel 2002). Between 1800 and 1900 CE, $\delta^{13}\text{C}$ 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, $\delta^{13}\text{C}$ 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, $\delta^{13}\text{C}$ 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 $\delta^{15}\text{N}$ 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, $\delta^{15}\text{N}$

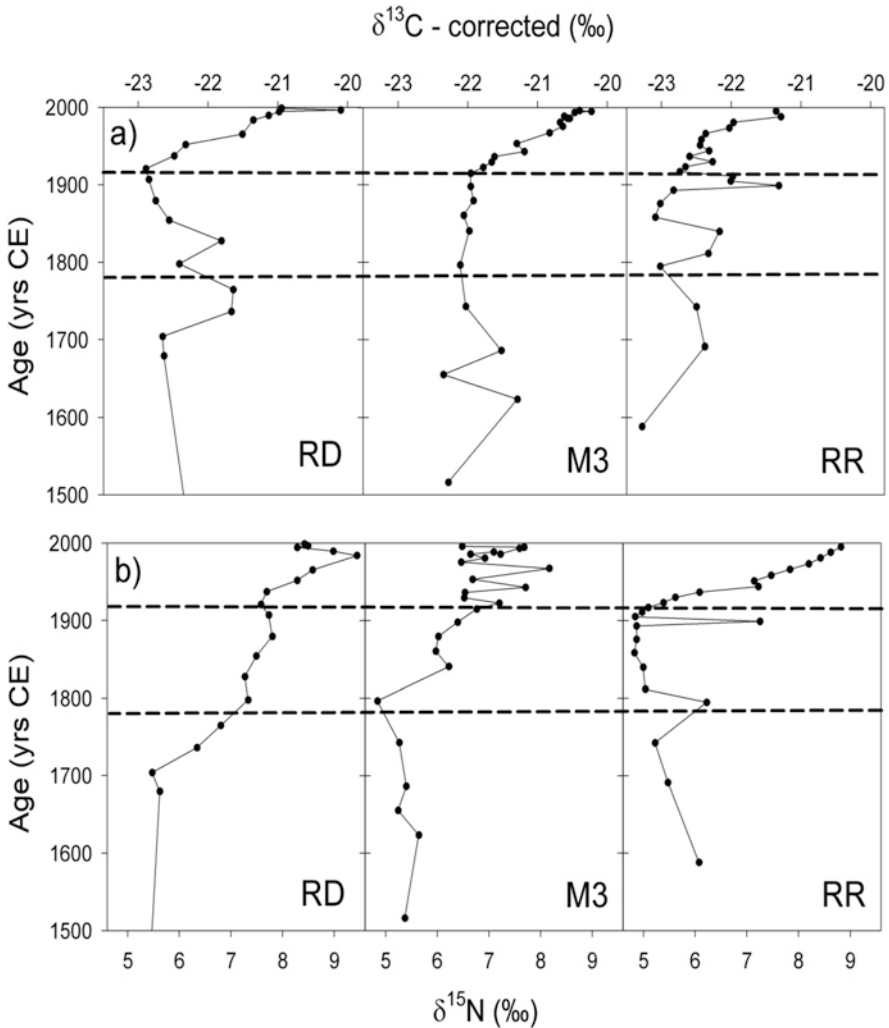


Fig. 9 Stable isotope profiles in three sediment cores collected from the mesohaline region of Chesapeake Bay. Reprinted with permission by the American Society of Limnology and Oceanography. Copyright (2002) by the American Society of Limnology and Oceanography, Inc.

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 $\delta^{15}\text{N}$ 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, $\delta^{15}\text{N}$ values do not increase until around 1900 CE. The timing of these $\delta^{15}\text{N}$ 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, ^{15}N 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 $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ records to longer timescales. For example, in this study, sediment core profiles of $\delta^{13}\text{C}$ 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 $\delta^{13}\text{C}$ values, were identified around 1935, 1800, 1560 CE, and 970 and 300 before CE (BCE).

In another study, negative $\delta^{13}\text{C}$ 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 long-term shifts in the strength of North Atlantic thermohaline circulation.

$\delta^{15}\text{N}$ signatures, recorded in a core collected from a freshwater wetland, were used to examine responses to changing land use and population in the Bay watershed over the past 350 years (Elliott and Brush 2006). $\delta^{15}\text{N}$ values ranged from 1.7 at the base of the core, consistent with isotopic signatures associated with biological N fixation, to 6.9 per mil in the surface horizons. Increasing values of $\delta^{15}\text{N}$ over time were coincident with two changes to the Bay watershed: (1) the transition from forested conditions during initial (1650 CE) and peak (1880 CE) land clearance, and (2) enrichments in $\delta^{15}\text{N}$ due to population growth and increased delivery of wastewater nitrogen. An important finding from this study was that anthropogenic activities in the watershed may have disproportionate influences on adjacent aquatic systems, depending on the extent to which the systems are connected hydrologically.

5.3 *Organic Biomarkers in Chesapeake Bay*

Organic biomarkers were also examined in the cores collected by Zimmerman and Canuel (2002) to understand changes in the flux of OM and its source composition. Mass accumulation rates were determined using ^{210}Pb and ^{137}Cs geochronologies and total organic carbon (TOC) was measured downcore using an elemental analyzer. Combining this information, TOC accumulation rates were calculated for each of the three cores. TOC accumulation rates showed increased rates of TOC accumulation, beginning in the early nineteenth century, at two of the sites (RD and

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.

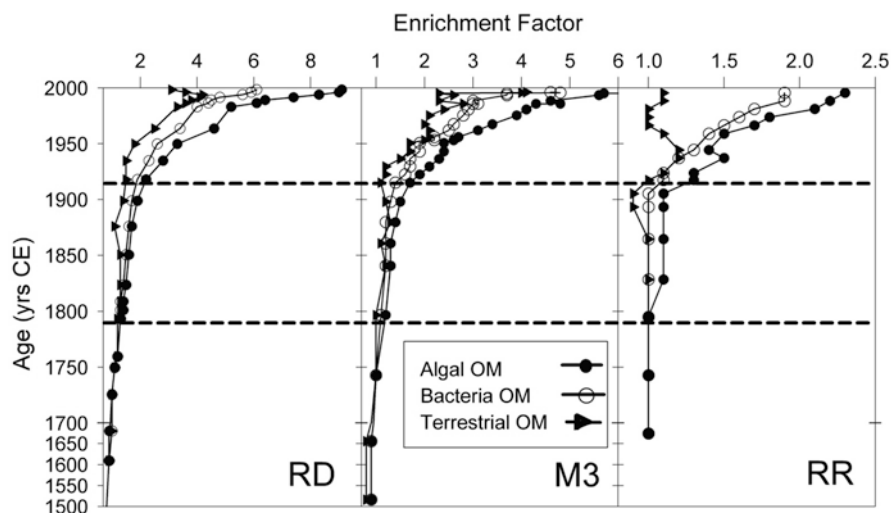


Fig. 10 Sediment core profiles showing enrichment factors for algal, bacterial and terrestrial organic matter calculated from organic biomarkers. Reprinted with permission by the American Society of Limnology and Oceanography. Copyright (2002) by the American Society of Limnology and Oceanography, Inc.

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 $\delta^{13}\text{C}$ 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). Paleoecological approaches can provide managers and policy makers with an understanding of the Bay's responses to

climate change in the historical and geological past. Additionally, the historic record provides information about the interactions between land use and climate. This information will be useful for predicting future responses to climate change as well as the development of effective goals and strategies for water quality and environmental management. A challenge for the future will be to predict how large-scale problems, such as nutrient loadings and eutrophication, will interact with anticipated changes in climate.

In Chesapeake Bay, paleoecological studies have provided numerous insights about how the Bay has changed over time in response to both anthropogenic and climatic processes. Throughout this chapter we provide examples of the application of paleoecological proxies to the Chesapeake Bay system. These approaches are also applicable to other estuaries, providing an opportunity to better understand how these dynamic regions respond to climate change and anthropogenic activities. This chapter also reviews some of the cautions and considerations that must be applied when conducting paleoenvironmental studies. Future work should be directed at the development and validation of new approaches and proxies, new combinations of existing methodologies (e.g., organic biomarkers combined with pollen or microfossil studies and combined use of organic and inorganic proxies), and increased collaboration between the disciplines of ecology, hydrology, geology and biogeochemistry.

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