

Sediment geochemical records of eutrophication in the mesohaline Chesapeake Bay

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Abstract

An organic geochemical analysis of sediments in three cores from the mesohaline Chesapeake Bay was carried out to reconstruct the progression of eutrophication and anoxia/hypoxia over the past five centuries. Evidence of eutrophication was found in the stable isotopic and lipid biomarker signatures of organic matter in sediments of these cores beginning in the late 18th and early 19th centuries and continuing to the present. Enrichments in the carbon and nitrogen isotopic signature of these sediments likely result from enhanced primary productivity and nitrogen recycling, respectively, and occur, coincidentally, with increased fluxes of total organic carbon (TOC) and episodic enrichments (relative to TOC) of algal and bacterially derived lipid biomarker compounds. More extreme and enduring changes from the late 19th century to the present are indicated by up to fivefold increases in TOC accumulation and 2- to 10-fold enrichments (relative to TOC) in algal and bacterially derived lipid biomarker compounds. Increased dinoflagellate and other nondiatom algae relative to diatom production is indicated by lipid biomarker compound ratios. Increases in the ratio of acid-volatile sulfur to chromium-reducible sulfur in sediment indicate the first occurrence of anoxia/hypoxia in 1790 at the deepest site (26 m), and in 1915 at a site 15 m deep. The history of Chesapeake Bay productivity is reconstructed using a diagenetic model to estimate the amount of TOC and biomarker compounds lost to degradation. It is estimated that both TOC delivery and algal and bacterial production have increased by 150% or more relative to pre-Colonial times with a temporal progression similar to anthropogenic alteration of the watershed.

Research has shown that recent increases in net primary production (eutrophication) in temperate estuaries and coastal ecosystems have occurred (e.g., Cooper and Brush 1991, 1993; Barmawidjaja et al. 1995; Zimmerman and Canuel 2000) and are caused, in large part, by increased loadings of nitrogen (Nixon 1995; Vitousek et al. 1997). Seasonal anoxia/hypoxia is linked to eutrophication because oxygen is consumed during the respiration of organic matter (OM) produced in nutrient-enriched waters. While rivers deliver the majority of new nutrients to estuarine and coastal environments, freshwater inflow can also lead to a strengthening of water column stratification that effectively isolates deeper waters and limits oxygen renewal. Because the history of anthropogenic alteration of the Chesapeake Bay (CB) watershed, including the clearance of land for agriculture (which may have led to increased freshwater/nutrient inflow) and the utilization of inorganic nutrients as fertilizers, is well

documented, an examination of the progression of eutrophication and anoxia in CB can lead to a better understanding of the effects of anthropogenic activities on coastal systems.

At one site in the mesohaline CB (M3), increases in total organic carbon (TOC; Cornwell et al. 1996), phytoplankton- and bacteria-derived lipids, biogenic silica, and changes in sulfur speciation indicate an advancement of eutrophication and bottom water hypoxia/anoxia in the early 20th century (Zimmerman and Canuel 2000). Because major increases in the availability and application of fertilizers occurred in the CB watershed at the same time, a possible link between eutrophication and nutrient run-off was inferred. However, low dissolved oxygen concentrations, as well as increased primary production, may lead to enhanced preservation of organic matter (OM, TOC, and individual organic compounds; Lee 1992; Harvey and Macko 1997). It was therefore difficult to determine whether OM delivery or OM preservation had increased at site M3.

To resolve this question and to provide greater geographic coverage, additional sediment cores were collected from sites in the mesohaline CB likely to have experienced variations in the timing and intensity of anoxia/hypoxia. Carbon and nitrogen stable isotope data and additional dating and sediment accumulation rate data were collected as part of this study. These measurements were integrated with quantitative diagenetic models to reconstruct a regional record of paleoproductivity. By extending the spatial and temporal coverage of the eutrophication and anoxia record of CB, a better understanding of their causes and effects on the composition of OM delivered to CB sediments can be achieved.

Materials and methods

Study sites and sample collection—Sediment cores were collected at three sites in the mesohaline CB: RD, RR, and

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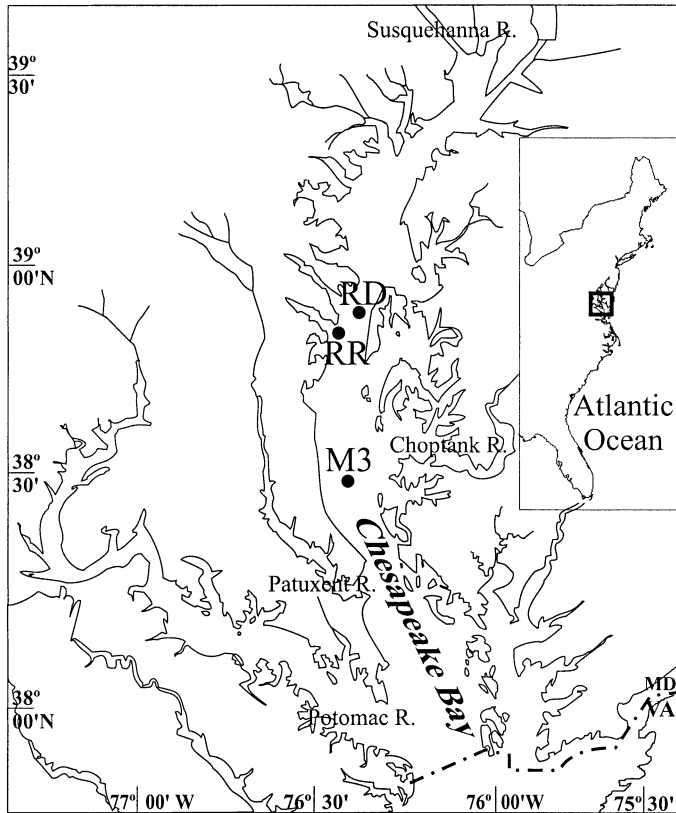


Fig. 1. Map of northern Chesapeake Bay showing core collection locations.

M3 (Fig. 1; Table 1). Located downstream from the turbidity maximum and far upstream of the bay mouth, it is likely that this region receives little exotic material and therefore reflects only the internal processes of the Bay. Because the highest productivity and greatest depths are found in this portion of the Bay, one might predict that the earliest signs of anoxia and eutrophication would occur here. Cores were collected using a 3 m-long kasten corer that, because of its large cross-sectional area (13×13 cm), minimizes compaction and disturbance of the sediment during sample collection. At site RD, a 4.5 m piston core was also collected, and the lower portion of this core (>3.0 m) was used to extend the depositional record for this site. Cores were sectioned into 2 cm intervals within 24 h of core collection. After homogenization, separate portions of sediment were placed into precombusted glass jars for organic and inorganic analyses (stored frozen at -80°C and -20°C , respectively) and in plastic centrifuge tubes for radioisotopic analyses.

Analytical methods—Sediment TOC was analyzed using a Fisons Instruments (EA1108) elemental analyzer after the removal of carbonate with HCl. Isotope ratio mass spectrometric analyses of oven-dried, HCl-acidified sediments were carried out at the University of California-Davis Stable Isotope Facility using a continuous flow system with on-line combustion (Europa Scientific Integra). Stable carbon and nitrogen isotopic values are expressed in standard delta notation relative to Pee Dee Belemnite and atmospheric N_2 standards, respectively. To correct $\delta^{13}\text{C}$ values for the -1.4 per mil depletion of atmospheric ^{13}C in atmospheric CO_2 due to fossil fuel burning since 1840 (Suess effect), we used an equation provided by Schelske and Hodell (1995) to calculate a time-dependent correction factor that was subtracted

Table 1. Summary of Chesapeake Bay sediment core locations and dating information.

	RD	M3	RR
Core location			
Latitude (N)	38°53.2'	38°43.1	38°52.7
Longitude (W)	76°23.5'	76°26.8	76°26.7
Collection Date	Nov 98 (USGS)	Mar 96 R/V <i>Bay Eagle</i>	Jun 98 (USGS)
Water depth (m)	26.5	15.0	7.9
Dating information			
Depth of anthropogenic Pb peak, 1975 (cm)	57	51	9
Anthro. Pb first appearance 1910 (cm)	183	101	23
Depth of ^{137}Cs penetration 1954 (cm)	93	6	18
Ragweed/Oak pollen increase 1850 (cm)	230	141	<23
Depth of excess ^{210}Pb penetration (cm)	147	101	25
Dating model (core horizon, cm)	0–75	75–200	200–450
Mean linear accumulation rate (cm yr^{-1})	4.16	2.08	0.80
Mean mass accumulation rate ($\text{g cm}^{-2} \text{yr}^{-1}$)	1.21	0.78	0.47
Sampling interval (cm)	2	5	10
Temporal resolution per interval (yr)	0.2	1.9	12.0
			0–50
			50–100
			>150
			0–100
			0.30
			0.14
			2
			6.5
			6.5

from the $\delta^{13}\text{C}$ value of each individual sample. Total Pb was extracted into HNO_3 and HCl and analyzed by flame atomic absorption spectroscopy. Duplicate analyses of the above parameters were performed, and a third analysis was carried out in cases where agreement was not within 10%. Sulfur speciation analyses were carried out according to the methods of Cornwell and Morse (1987) in which chromium-reducible and HCl-volatile portions are released as H_2S and quantified via Pb titration.

Lipids were extracted from 10 g wet sediment into chloroform:methanol (2:1, v/v) aided by sonication (repeated four times). Following saponification and extraction into hexane, the neutral and acidic (after methylation) lipids were purified by silica gel chromatography. Fatty acid methyl esters and trimethylsilyl ether derivatives of sterols and alcohols were quantified by gas chromatography (GC; Hewlett Packard 6890 with FID) by comparison of their peak areas to that of methyl heneicosanoate and 5 α -cholestane, respectively, added prior to GC analysis. Extraction efficiencies were corrected using myristyl arachidoate added prior to extraction. Peak identifications were confirmed using GC-mass spectrometry (HP 6890 GC-MSD). Further details regarding the analytical methods employed may be found in Zimmerman (2000).

Dating methods—Five dating tools were employed: ^{210}Pb , ^{137}Cs , ^{14}C , total Pb, and ragweed pollen. ^{210}Pb activity was measured by alpha spectroscopy (EG&G Ortec) following the methods of Nittrouer et al. (1979), in which the radiogenic daughter, ^{210}Po , was electrodeposited from an acid leachate onto a silver planchet. A ^{209}Po spike served as a yield determinant. Constant ^{210}Pb activities in the lower portions of the cores are assumed to represent supported Pb, and this value was subtracted from total activity to yield excess ^{210}Pb activity. Because the upper portions of each core displayed log-linear excess ^{210}Pb profiles when plotted against cumulative mass, constant sediment mass accumulation rates (MAR) could be calculated. For the lower portion of each core, MAR was determined for each interval as the slope on an age-cumulative mass power curve fit to sediment age horizons dated by the four non- ^{210}Pb dating tools.

^{137}Cs activity was measured on whole ground sediment in a well-type intrinsic germanium gamma detector (Princeton Gamma-Tech). The depth of ^{137}Cs penetration identifies the early atomic bomb testing sediment horizon of 1954 (Ritchie and McHenry 1990). Total Pb concentration profiles were used to identify the 1910 and 1975 sediment horizons (the start of the industrial revolution and end of the use of leaded gasoline in the U.S., respectively; Graney et al. 1995). Palynological, microfossil and ^{14}C dating information were provided to us by D. Willard and T. Cronin of the USGS (Reston, Virginia) and S. Coleman of the USGS (Woods Hole, Massachusetts), respectively. The highest ragweed to oak pollen grain ratio in each core was used to identify the mid-19th century period of greatest land clearance in the watershed.

Data analysis—Although 65 fatty acids (FAs) and 24 sterol compounds were identified in the CB core sediments, a few were chosen for interpretation because of their greater

relative abundance, our confidence in their identification, and their association with likely sources of OM to CB sediments. Biomarker assignments for this system were aided by previous research on the distributions of FA and sterol compounds in CB surface sediments and monocultures of common algal groups in CB. This work, along with a table of biomarker source assignments with full citations, is presented in Zimmerman (2000) and Zimmerman and Canuel (2001).

Lipid biomarker data were normalized to the TOC content of each sample to minimize between-site or temporal changes in the amount of OM deposited or preservation conditions. Thus, changes in carbon-normalized biomarker concentrations represent enrichments/depletions in specific OM sources relative to sediment TOC. Mass fluxes of a geochemical species were calculated as the product of sediment MAR and the weight percentage of each species.

Diagenetic models—It is particularly important when using organic geochemical indicators to reconstruct the recent past (the period in which degradation rates are the greatest) to consider the role of diagenesis in altering the geochemical record of environmental change. We use two approaches. In the first, we construct steady-state diagenetic models that are compared with observed geochemical profiles. By doing so, we can answer the question: Is the system at steady-state or has some environmental change occurred? We have found the most reasonable model to be that of Middelburg (1989), which incorporates a time-dependent apparent degradation rate parameter $k = 0.16t^{-0.95}$ (incorporating both experimental and field data), into the more familiar 2-G decay models of Berner (1980). For some metabolizable organic component of concentration C_m deposited at time t

$$C_m = C_{m_0}e^{-kt} + C_\infty \quad (1)$$

where C_{m_0} represents the surface sediment (initial) concentration of the metabolizable component and C_∞ is the concentration of the nonmetabolizable organic component (the vertical asymptote of the C_m profile). The modeled flux of an organic component to the sediment is calculated as the product of its modeled concentration and sediment MAR for a particular sample.

We use a second approach to correct our organic component concentrations for the degradative loss that can be estimated to have occurred using the above equations and, thus, to construct a paleoproductivity proxy. The organic component lost to degradation for any sample deposited t years ago ($C_{\text{lost-}t}$) is estimated as

$$C_{\text{lost-}t} = C_{m_0} - C_{m_0}e^{-kt} \quad (2)$$

The degradation-corrected concentration ($C_{\text{corr-}t}$) for a sample of concentration C_{m_t} is then

$$C_{\text{corr-}t} = C_{m_t} + C_{\text{lost-}t} \quad (3)$$

The time-dependant degradation rate parameter k of Middelburg (1989) is used in Eq. 2 for TOC. The time versus k relationships used for total FAs ($\log k = -0.914 \times \log t - 0.002$) and total sterols ($\log k = -1.12 \times \log t - 0.065$) were derived by Canuel and Martens (1996) for sediments deposited over the past 200 yr in a variety of systems. The

assumptions that the concentration of these biomarker compounds in their respective sources have remained constant over time and that there has been no change in the extent of remineralization within the water column prior to deposition are implied.

A focusing factor was calculated for each core by comparing the inventory of excess ^{210}Pb in each core to the expected inventory based on the sources of the isotope (34 dpm cm^{-2} ; Helz et al. 1985) to the Bay. The degradation-corrected TOC flux is then divided by the focusing factor calculated for that core so that the consistency of the record among the cores can be evaluated. It is assumed that the extent of sediment focusing has remained constant over the time period represented by these sediments. Degradation-corrected lipid biomarker flux data are not focusing-corrected, but instead, each flux was normalized to the average pre-1790 flux in each core and then OM source delivery factors were calculated as the mean of their respective biomarker compounds (all those shown in Fig. 3 except cholesterol) for each OM source (algal, bacterial, and terrestrial). Tables and graphs of the data at each intermediate stage of these calculations can be found in Web Appendix 1 (<http://www.aslo.org/lo/toc/vol.47/issue.4/1084a1.pdf>).

Results and discussion

Sediment accumulation rate—X-radiographs of each core revealed no evidence of major biologic or physical disturbance of the sediments. Distinct laminations and logarithmically decreasing ^{210}Pb activity profiles in the RD and M3 cores indicate no upper mixed layer due to bioturbation or resuspension and no hiatuses. The RR sediment core, however, while having a log-linear ^{210}Pb profile, visible horizontal striations, and shelly debris layers, was not laminated and could, therefore, suffer from episodes of sediment resuspension or small-scale (<1 cm) vertical mixing (bioturbation). The accumulation rate calculated for the RR site is, therefore, a maximal rate because of the possibility of downward mixing. These X-radiographs, as well as detailed tables of the data presented in this manuscript, are accessible in Web Appendix 1.

The constant MAR of $1.21 \text{ g cm}^{-2} \text{ yr}^{-1}$ ($r^2 = 0.89$), $0.47 \text{ g cm}^{-2} \text{ yr}^{-1}$ ($r^2 = 0.95$), and $0.14 \text{ g cm}^{-2} \text{ yr}^{-1}$ ($r^2 = 0.95$) were obtained for the upper portions of the RD, M3, and RR cores, respectively (Table 1). ^{137}Cs and total Pb-derived dated horizons in the upper portion of each core are consistent with the MAR values derived using ^{210}Pb . At the two deepest sites, RD and M3, sediment MAR has increased two- to threefold since European settlement, in agreement with findings of other workers (Donoghue 1990; Cooper and Brush 1993). A ^{14}C age of 1,521 yr at a depth of 350 cm in the RR core (Colman et al. 2002), however, indicates that a constant MAR of $0.14 \text{ g cm}^{-2} \text{ yr}^{-1}$ may be applied to the whole of the core.

TOC record—Sediments of all three cores deposited prior to 1790 are of low and constant TOC content (mean \pm SD, 1.58 ± 0.07). A gradual increase in percent TOC begins about 1790, followed by an abrupt increase to 2.3 to 3.7% between 1880 and 1915 at the RD and M3 sites and slightly

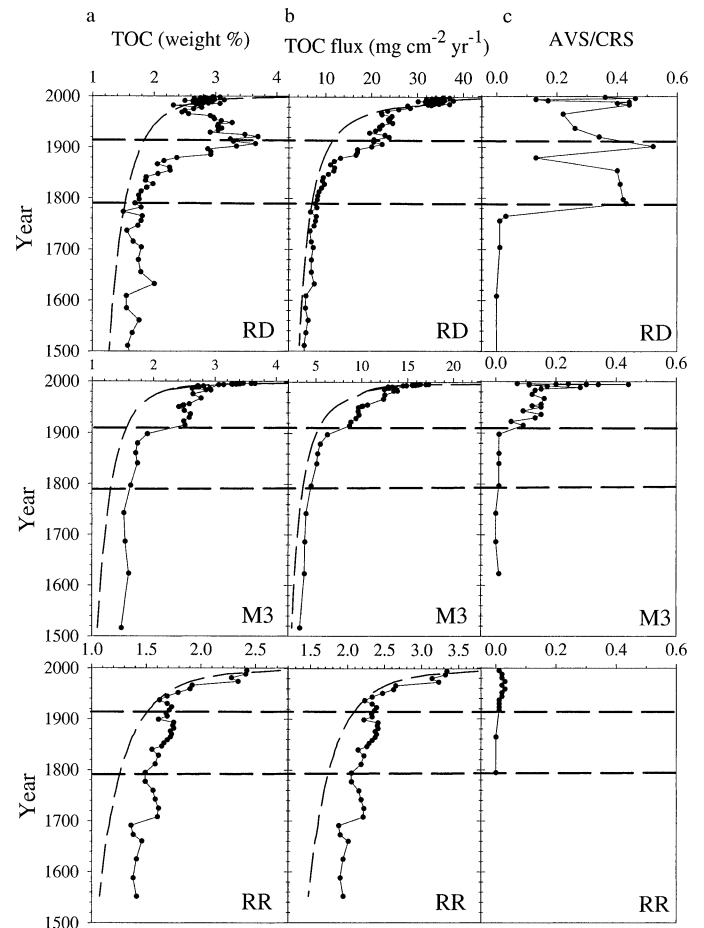


Fig. 2. Downcore record of (a) total organic carbon accumulation (weight %), (b) calculated mass flux ($\text{mg cm}^{-2} \text{ yr}^{-1}$) of total organic carbon, and (c) ratio of acid-volatile sulfur to chromium-reducible sulfur (AVS/CRS) in three Chesapeake Bay cores. Horizontal dashed lines at years 1790 and 1915 indicate horizons at which major geochemical changes occur. The dashed lines plotted in panels a and b are modeled diagenetic profiles of TOC (%) and TOC-MAR using a time-dependent degradation rate parameter (see Methods section).

later (1945) at the RR site (Fig. 2a). Unlike the percent TOC record, the calculated mass flux of organic carbon (TOC-MAR) increases continually from the base of the record toward the sediment surface in all three cores (Fig. 2b). Relative to the years prior to 1790, the mean TOC-MAR are 2.2-, 1.4-, and 1.1-fold greater between 1790 and 1915 and 4.7-, 3.6-, and 1.3-fold greater after 1915 at the RD, M3, and RR sites, respectively.

Only the percent TOC and TOC-MAR profiles of the RR core resemble hypothetical diagenetic profiles, suggesting that they may be the result of steady-state degradation alone. Data from the RR core should be interpreted with caution because its postdepositional history is uncertain. However, it is presented to serve as an example of the possible influence of local environment on the geochemical record. Organic carbon in excess of that which can be attributed to steady-state degradation or a changing sediment MAR (of constant OM concentration) is present in RD and M3 sedi-

ments deposited since the mid-1800s. This conclusion is supported by step-like upcore increases in both percent TOC and TOC-MAR profiles and upcore increases in elemental TOC:total N ratios (data not shown) in sections of all three cores, which are not typical of diagenetic profiles.

In addition to an increase in the delivery of organic matter to the sediment, the observed trends in percent TOC and TOC-MAR might be attributable to enhanced OM preservation due to increased sediment MAR (Henrichs and Reeburgh 1987) or decreased bottom water dissolved oxygen concentration (e.g., Lee 1992). However, there is no evidence for an abrupt change in sediment MAR at any time at any of the sites. The redox history at each of these sites is provided by the ratio of acid-volatile sulfur to chromium-reducible sulfur ($AVS/CRS = FeS/FeS_2 + S^0$; Roden and Tuttle 1993) that is similar to the traditionally used "degree of pyritization" but is less dependent on Fe availability. Higher AVS/CRS ratios indicate an increase in the prevalence or intensity of anoxia/hypoxia beginning in 1790 at RD and 1915 at M3 (Fig. 2c), which is broadly consistent with the CB redox history developed by Karlson et al. (2000) and Adelson et al. (2001) using trace metals and benthic foraminifera, respectively. The decreases in water column oxygen concentration occur much earlier than the increase in TOC delivery at site RD and slightly later than that of site M3. Increased TOC deposition might have occurred at site RR during the 20th century, although there has been no occurrence of anoxia/hypoxia or change in sediment MAR at this site. Enhanced water column productivity is, therefore, the most likely mechanism for the increase in sediment OM content as well as the cause of water column oxygen depletion.

Lipid indicators—Most autochthonously derived compounds (plankton and bacterial biomarkers) display similar patterns of enrichment relative to TOC; low concentrations before 1750, periodic increases during the late 18th and 19th century at the RD and M3 sites, and progressive increases during the 20th century in all cores (Fig. 3). For example, 24-methylcholesta-5,24(28)-dien-3 β -ol ($28\Delta^{5,24(28)}$), a compound usually associated with diatoms (Volkman 1986), is enriched relative to TOC by varying amounts (up to fourfold) in sediments of all cores deposited after 1915 and by 50% in RD sediments between 1750 and 1850 relative to earlier periods. C_{20} and C_{22} polyunsaturated fatty acids (ΣC_{20+22} PUFA) occur in a variety of phytoplankton and zooplankton (Volkman 1986) and display a similar enrichment pattern, although these compounds are more variable, most likely because of the greater reactivity of this compound class. Relative to the pre-1790 period, the average enrichment of 4 α ,23,24-trimethyl-5 α -cholest-22-en-3 β -ol ($30\Delta^{22}$), derived mainly from dinoflagellates (Nichols et al. 1984; Volkman 1986), is about two- and fourfold between 1790 and 1850 and four- and sevenfold after 1915 in the RD and M3 cores, respectively. Again, the RR core shows no enrichment until after 1915. Similarly, cholest-5-en-3 β -ol ($27\Delta^5$), the dominant sterol in zooplankton, found in some algae as well (Volkman 1986), is enriched only in the post-1915 sediments of all three cores. All of these plankton biomarkers are increasingly enriched (by factors of 2–10) in

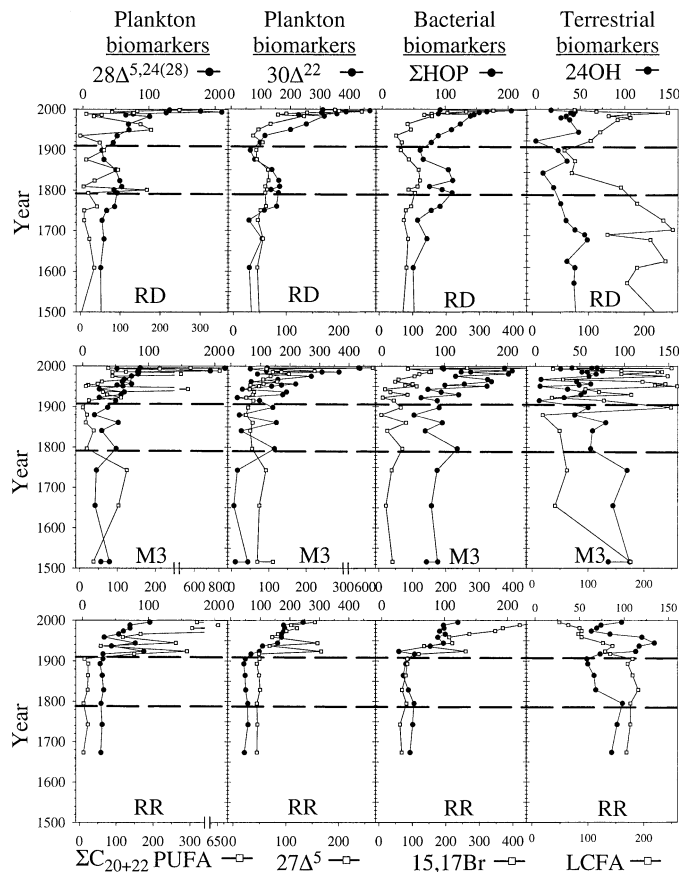


Fig. 3. Downcore profiles of TOC normalized lipid biomarker compound concentrations ($ng\ mg^{-1}\ TOC$) for biomarkers indicative of plankton, bacterial, and terrestrial OM sources (columns) in three Chesapeake Bay cores (rows). The upper scale of each graph applies to the four compounds listed at the top of the figure (closed circles) and the lower scale for the four compounds listed at the bottom of the figure (open circles). Note that scales differ between study sites. Keys to compound abbreviations are found in the text.

OM deposited after 1915. Similar enrichment patterns were found for algal biomarkers not shown here, such as brassicasterol, campesterol, and C_{18} and C_{16} mono- and polyunsaturated FA compounds that are mainly algal-derived (Zimmerman 2000).

Bacterially derived lipid biomarker compounds are also consistently enriched in OM deposited after 1915, and episodically during the 19th century, relative to previous periods. For example, *iso*- and *anteiso*-branched C_{15} and C_{17} FA (15,17Br), which are found in a variety of eubacteria, including sulfate reducers (Parkes and Taylor 1983; Kaneda 1991), are enriched relative to TOC by 2.5-, 2.8-, and 4.4-fold after 1915 in the RD, M3, and RR cores, respectively, and by about half that amount in the period between 1750 and 1850 relative to earlier periods. The hopanols (ΣHOP) are also found in a variety of bacteria (Cranwell 1982) and are similarly enriched in post-1915 sediments of all cores and between 1750 and 1850 at RD and some M3 sediments. After 1915, both of these bacterial markers (as well as the bacterial marker 10-methyl branched C_{16} FA) display progressive enrichments up to the present at all three sites.

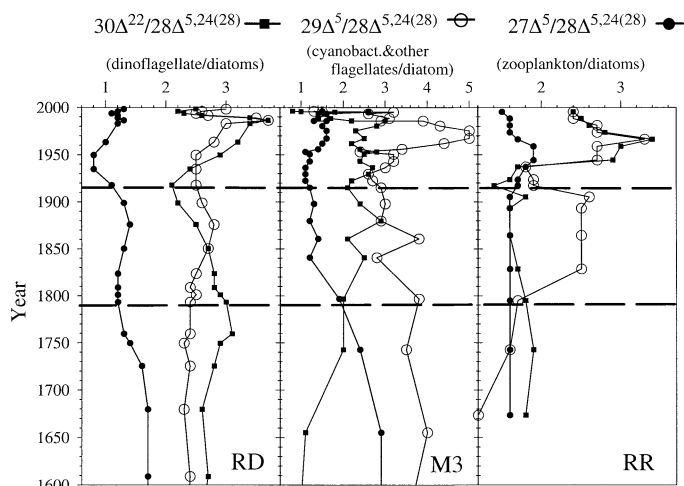


Fig. 4. Downcore profiles of $30\Delta^{22}$ (dinoflagellate sterol), $29\Delta^5$ (cyanobacteria and green flagellate sterol), and $27\Delta^5$ (zooplankton sterol) relative to $28\Delta^{5,24(28)}$ (diatom sterol).

Long-chain even-numbered FAs (LCFA; $>nC_{22}$) and C_{24} alcohol (24OH) have been used as indicators of terrestrially derived OM because these compounds are mainly derived from vascular plants (Cranwell 1982), although they been shown to occur at trace levels in some phytoplankton (Volkman et al. 1980). Downcore profiles of LCFA and 24OH display no easily discernible temporal trend in the RD and M3 cores. Overall, these compound profiles indicate that terrestrial OM contributions to TOC remained constant or decreased proportionally at these sites over the past five centuries. In contrast, there is an obvious decrease in LCFA in sediments deposited at the RR site since 1900.

Biomarker ratios can be used to assess changes in the relative predominance of phytoplankton groups. The influence of diagenesis is minimized by selecting compounds of similar reactivity. The ratio $30\Delta^{22} : 28\Delta^{5,24(28)}$, an index for the relative contributions of dinoflagellates versus diatoms to sediment OM, begins to increase during the late 18th century in some of the cores but shows major increases after 1915 in all cores (Fig. 4). Because we found the distribution of 24-ethylcholest-5-en- 3β -ol ($29\Delta^5$) in CB surface sediments to be similar to that of cyanobacteria and other nondiatom alga (mainly flagellates; Zimmerman and Canuel 2001), the $29\Delta^5 : 28\Delta^{5,24(28)}$ ratio provides an index for assessing the contributions of cyanobacteria and green flagellates relative to diatoms in CB. Although the timing differs somewhat in each core, increases in this ratio beginning in the 19th century and progressing throughout the 20th century suggest a relative increase in small-celled phytoplankton over this time period. At both RD and M3, ratios of $27\Delta^5 : 28\Delta^{5,24(28)}$ have decreased since 1790, indicating decreasing contributions of OM from zooplankton relative to diatoms over the time frame represented by our cores. Other biomarker ratios examined, such as campesterol : $28\Delta^{5,24(28)}$ and $C_{18:1} : C_{16:1}$ FA support a similar interpretation (Zimmerman 2000).

The apparent change in community structure, from diatom to small-celled algae and from a "classic" metazoan food web (greater zooplankton abundance) to one dominated by microbial recycling of OM, has been hypothesized to occur

in systems experiencing severe eutrophication (Marshall and Lacouture 1986; Verity 1988). Diatoms often dominate under conditions of increased nutrient availability (e.g., Sanders et al. 1987), such as may have occurred in the late 1700s with early land clearance and increased runoff. However, as nutrient concentrations increase further, diatoms may no longer have a competitive advantage and likely become silica limited.

A number of lines of evidence indicate that the observed biomarker compound profiles are not the result of steady-state diagenetic processes but, instead, represent increasing fluxes of autochthonous OM to the sediment. Zimmerman and Canuel (2000) presented detailed evidence for this for the M3 core, and similar results are found here for the RR and RD cores. Specifically, the ratio of many lipid compounds or compound classes of different reactivities remains relatively constant throughout each of the cores. Downcore increases in the FA : sterol ratio in some sections of the cores are, in fact, the opposite of an expected diagenetic trend because of the greater reactivity of FAs as a whole (Sun and Wakeham 1994).

The slope of a plot of the natural logarithm of a compound concentration against time is the apparent decay rate parameter k (by rearranging Eq. 1) for that compound. For plankton and microbially derived FA and sterol compounds in each core, a change in slope occurs between 90 and 120 yr BP (k generally $< -0.01 \text{ yr}^{-1}$ in the upper core and $> -0.003 \text{ yr}^{-1}$ in the lower core). Either an increase in the decay rate or an increased influx of these biomarker compounds has therefore occurred between 1880 and 1910. The latter is suggested by the similarity in k values across compound classes and among the different cores within similar time periods.

Isotope record—A positive excursion in both the carbon and nitrogen isotopic signatures of sediment OM occurs first in the more northerly portions of the mid-Bay (at RD in 1736; at RR in 1790) and somewhat later ($\delta^{15}\text{N}$ in 1840; $\delta^{13}\text{C}$ in 1900) further south at M3 (Fig. 5). The lipid biomarker data indicate no change in the relative contribution of terrestrially derived OM to these sites, and diagenesis does not alter the sedimentary stable isotope signature of carbon (Meyers 1994). We interpret the 0.5 to 2‰ increases in $\delta^{13}\text{C}$ through time as evidence of increasing primary productivity in surface waters and associated carbon limitation (e.g., Schelske and Hodell 1995; Hodell and Schelske 1998) or to increasing relative contributions of phytoplankton-derived OM to the sediment. In support of the latter interpretation, sedimentary $\delta^{13}\text{C}$ (and not the $\delta^{15}\text{N}$) signature is positively correlated to carbon-normalized abundances of plankton-derived lipid compounds (generally, $r = 0.70\text{--}0.95$; $P < 0.001$) in each core.

Enrichments in ^{15}N (1.0–2.5‰) begin concurrently with those for ^{13}C and autochthonous biomarker enrichments but, in contrast, increase continuously since the early 19th century (Fig. 5). The $\delta^{15}\text{N}$ record is more difficult to interpret because of the greater number of biogeochemical processes influencing nitrogen. Higher productivity could cause ^{15}N enrichment due to nitrogen depletion, but this is unlikely since nitrogen loadings have presumably increased. Domestic sewage is also a possible source of isotopically enriched nitrogen

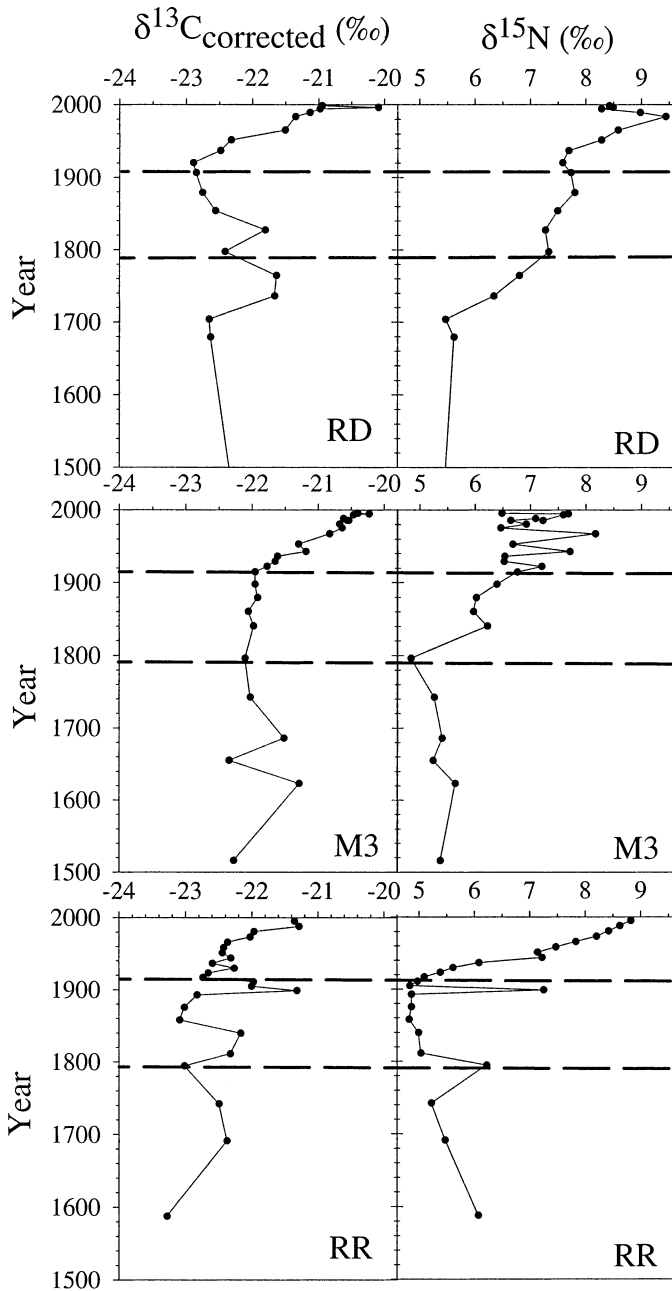


Fig. 5. Downcore record of stable carbon and nitrogen isotopic signature of OM in three Chesapeake Bay core sediments. $\delta^{13}\text{C}$ signatures are corrected for the Suess effect (see Methods section).

(5–20‰; Heaton 1986). Although it cannot be ruled out, we found no lipid indicators of sewage-derived OM in these sediments (i.e., coprostanol). Soil nitrates may be ^{15}N enriched (3–12‰; Heaton 1986), and their release to the estuary could be caused by erosion resulting from increases in agriculture and development. However, absolute concentrations of lipid biomarkers for terrestrially derived material are constant throughout the cores. Alternatively, the microbial processes of nitrification and denitrification remove isotopically light nitrogen, leaving an enriched pool of NH_4^+ that is preferentially utilized by phytoplankton in CB and other

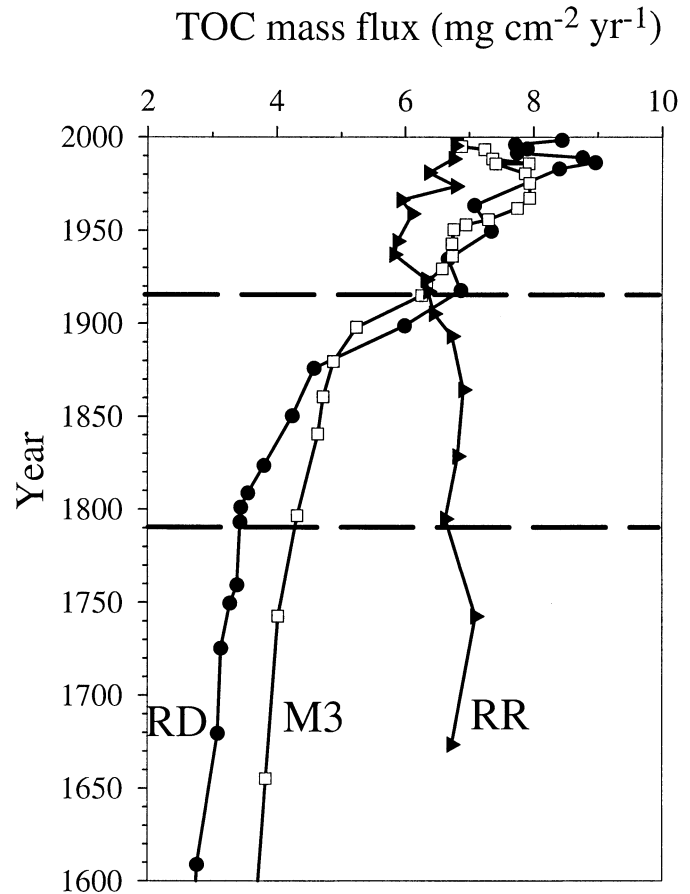


Fig. 6. Downcore profiles of TOC mass flux ($\text{mg cm}^{-2} \text{yr}^{-1}$) in three Chesapeake Bay cores. TOC mass fluxes have been corrected for degradation and between-site differences in sediment focusing (focusing factors of 4.3, 2.5 and 0.5 for RD, M3, and RR, respectively).

estuaries (Mariotti et al. 1984). These processes may be stimulated by high nitrogen and carbon loadings (Seitzinger 1990; Kamp-Nielsen 1992). In support of this explanation, the most ^{15}N -enriched surficial sediments are found in the midregion of CB (Zimmerman and Canuel 2001), where both sediment TOC and benthic ammonium regeneration rates are the highest (Boynton and Kemp 1985). Thus, the increase in $\delta^{15}\text{N}$ that first occurs in the late 1700s suggests a shift toward enhanced OM recycling stimulated by increased nutrient loading and the resultant primary productivity in the mesohaline CB.

Paleoproductivity estimation and implications—The degradation and focusing-corrected TOC-MAR profiles indicate continuously increasing delivery of organic carbon since the early 19th century at sites RD and M3 (2.5- and 2-fold increase, respectively; Fig. 6). The greatest rate of increase in TOC delivery occurs between 1880 and 1950 at these sites (about 1.5-fold increase during this period alone). The delivery of TOC appears to have remained constant or decreased somewhat since 1980. After applying the degradation and sediment focusing corrections, the TOC records at the RD and M3 sites are consistent, similar in both timing

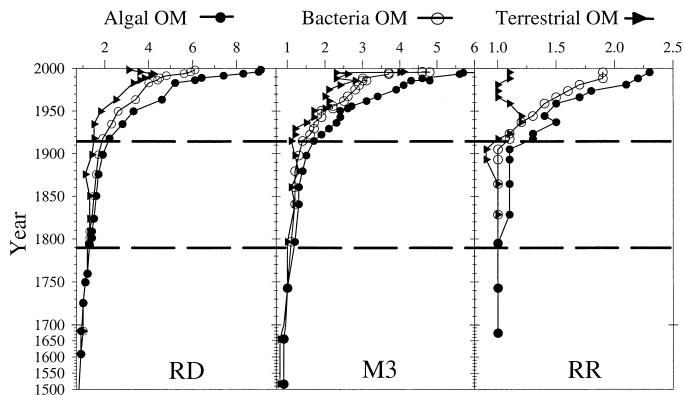


Fig. 7. Downcore profiles of degradation-corrected OM delivery factors for OM derived from phytoplankton, bacterial, and terrestrial sources in three Chesapeake Bay cores. Delivery factors are expressed relative to mean values for the lower horizons of each core (pre-1790) and smoothed by a three-point moving average.

and magnitude. No change in TOC flux is observed in the RR core, in line with previous suggestions that the carbon profiles at this site may be controlled by steady-state diagenesis. The much lower ^{210}Pb inventories at this site might also indicate that portions of the record have been lost or influenced by postdepositional resuspension or some other physical disturbance.

Another paleoproductivity proxy—degradation-corrected OM delivery factors—indicates that since the late-18th century and particularly during the 20th century, the mesohaline region of CB has received increasingly greater inputs from algal and bacterially derived OM sources (Fig. 7). These calculations allow us to hindcast a 1.5- to 2-fold increase in the delivery of algal and bacterially derived OM to CB sediments during the 19th century and as much as a 2- to 6-fold increase during the 20th century relative to pre-19th century periods. Extremely high estimates of source delivery increases during the past two decades, however, are probably inaccurate because of the variability in degradation rates for various compounds and environments during this time. A median estimate of about a 2.5- to 4-fold increase overall in the delivery of algal and bacterially derived OM, with the former greater than the latter, is reasonable and consistent with the TOC record.

A smaller (1.5- to 3-fold) increase in the delivery of terrestrially derived OM to the RD and M3 sites during the 20th century is also indicated. Because this increase is roughly the same as the increase in sediment delivery to these sites, the proportion of terrestrially derived OM in the sediment has remained constant or decreased. This may be due, in part, to the construction of dams on the Susquehanna River in the late 1920s. In contrast, since the beginning of the 19th century, sediments of the mesohaline Bay have become progressively enriched in algal and bacterially derived OM.

It has been estimated that historical nitrogen loading from all sources, including runoff and atmospheric deposition since European settlement, has increased three- to eightfold to CB (Boynton et al. 1995; Jaworski et al. 1997) and other eastern U.S. estuaries (Jaworski et al. 1997; Nixon 1997).

Mesocosm enrichment studies and interestuary comparisons indicate that this change in nutrient loading would lead to roughly a doubling in the rate of primary productivity for the Bay as a whole (Nixon 1997). By analyzing measurements of chlorophyll *a* concentration taken over the past 50 yr in CB and removing the effects of freshwater flow, Harding and Perry (1997) estimated that phytoplankton biomass had increased by a factor of about 2 to 2.5 in the mesohaline region of the Bay. Our most conservative estimate of a 2.5-fold increase in the delivery of autochthonously derived OM to the mesohaline CB is similar to these estimates.

Given the current annual average primary productivity in CB of $350 \text{ g C m}^{-2} \text{ yr}^{-1}$ (Baird and Ulanowicz 1989), we can then estimate the pre-eutrophication productivity to have been about $140 \text{ g C m}^{-2} \text{ yr}^{-1}$. However, a higher figure would be calculated if autotrophic bacterial (cyanobacteria) production, which also may have increased 2.5-fold, were included. A shift in phytoplankton composition toward groups of smaller cell size may have resulted in a greater degree of water-column remineralization, thus biasing the estimate downward. If, on the other hand, anoxic/hypoxic conditions have led to a decrease in the extent of water-column remineralization, this figure could be an overestimate.

Although human population and land clearance in the CB watershed have increased since the 17th century, evidence of environmental disturbance caused by resultant nutrient influx and freshwater runoff do not begin to appear until the late 18th century. Sediments deposited during the early 19th century reflect periodic eutrophication and anoxia in the deepest portions of the Bay. After this time, periods of advancing anthropogenic alteration of the watershed correspond to observed changes in the quantity and quality of OM delivery to CB sediments. The rate of land clearance increased in the 1880s with the introduction of dynamite for blasting of stumps and again in the 1920s with mechanization (Williams 1989). With the Guano Island Act of 1856 and the discovery and development of phosphate mines in South Carolina in 1867, the 1870s saw the first intensive use of these organic fertilizers in eastern Virginia and Maryland (Wines 1985). Between 1860 and 1880, the number of factories processing these so-called “superphosphates” nearly quadrupled, and Baltimore, Maryland, was the center of this industry (Wines 1985). Although synthetic fertilizers were first commercially available and used in the 1920s, they did not see widespread use until the 1950s (Nixon 1995). It is at this time that the estuary entered a state of advanced eutrophication that is reflected in the quantity and quality of sedimentary OM of the mid-Bay.

Although the large-scale temporal progression of eutrophication in the mesohaline region of CB mirrors the history of increasing land clearance and fertilizer use, the decadal-scale timing of the onset of eutrophication and anoxia may be dictated by the occurrence of climate-related periods of increased freshwater inflow. The periods in which we find evidence of increased productivity (i.e., late 1700s and late 1800s to early 1900s) were periods of above-average freshwater input to the Bay, as indicated by precipitation and stream discharge records, and lower bay water salinities, as reconstructed by microfossils (Cronin et al. 2000) and tree-

ring chronologies (Stahle et al. 1998). The onset of eutrophication and anoxia might have been stimulated by wet periods that carried new nutrients into the Bay and increased stratification. During the later 20th century, however, even years of average runoff carry enough nutrients to supply these higher levels of productivity.

The multiproxy approach employed in this study combines stable isotopic and bulk geochemical information and organic biomarker analysis across multiple compound classes, allowing us to reconstruct a history of anthropogenic disturbance of a coastal system with a level of detail and confidence unattainable with any of these methods alone. In addition, we have found that the calculation of OM fluxes using multiple sediment dating tools and the method presented here for correcting TOC and biomarker compound concentrations for degradative loss is necessary and instructive when working at these timescales.

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