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A geochemical record of eutrophication and anoxia in Chesapeake Bay sediments: anthropogenic influence on organic matter composition

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Abstract

Organic and inorganic geochemical indicators were examined in a 3-m core collected from the mesohaline region of Chesapeake Bay (CB) to determine how sources of organic matter (OM) have changed during the preceding three centuries of increasing anthropogenic influence in this region. This study also establishes the history of eutrophication and anoxia/hypoxia and relates these processes to changes in OM deposition and preservation and to historical events within the Bay's watershed. The sediment record shows that a marked increase in organic carbon (35%–50%), biogenic silica (18%) and total sulfur (42%) occurs between 1934 and 1948. This transition is likely due to increasing anoxic/hypoxic bottom water conditions as indicated by an abrupt change in sulfur speciation. Lipid biomarker distributions indicate that a substantial change in the sources of OM deposited since 1934 has also occurred. Biomarker compounds derived from phytoplankton and microbial sources show a 2- to 4-fold increase in their abundance relative to total organic carbon (TOC) between 1948 and 1975. Using both diagenetic models and information on lipid reactivity, an effort is made to distinguish compositional changes due to changes in OM delivery (both quantity and quality) from changes that may be due to OM degradation. It appears that enhanced OM production in the mesohaline region of CB has contributed to the observed changes in quantity and character of OM preserved in sediments from this site. Increased inorganic fertilizer application and human population growth in the watershed are coincident with the onset of eutrophic and hypoxic conditions in CB, suggesting that anthropogenic activities within estuarine watersheds may exert a substantial influence on carbon cycling processes in estuaries and potentially the coastal ocean.

Keywords: Chesapeake Bay; organic carbon; estuaries; anaerobic environment; eutrophication; lipids

1. Introduction

Major changes have occurred in watersheds on the east coast of the United States since first settlement by Europeans in the mid-17th century. Along with progressive deforestation for agricultural development and the drainage of wetlands, industrialization and urbanization have transformed the landscape. Watershed alterations have had an effect on the environment and ecology of estuaries and the coastal zone globally. Cultural eutrophication (anthropogenically induced increases in primary produc-

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tivity) and resulting anoxic ($O_2 < 0.2$ mg l^{-1}) or hypoxic ($O_2 < 2.0$ mg l^{-1}) conditions are cited as amongst the most important environmental problems presently requiring scientific and political attention (Diaz and Rosenberg, 1995; Nixon, 1995). In addition to their harmful effects on organisms and ecosystems, changes in the frequency and intensity of low-oxygen events could have broader implications for global carbon cycling (Henrichs, 1992).

Episodes of deoxygenated waters have been observed in portions of Chesapeake Bay (CB), the largest estuary in the United States, as early as the 1930s (Newcombe et al., 1938). Since that time, the temporal and spatial extent of these events have increased progressively and have become a major environmental concern (Officer et al., 1984a). It is not known, however, to what extent deoxygenation events occur naturally in CB, or are purely anthropogenic in origin. Likewise, the primary cause of these events is not yet well understood. Both physical (i.e., stratification caused by increased freshwater runoff) and biological (i.e., enhanced OM production caused by increased nutrient inputs) factors may have contributed to the more frequent occurrence and greater intensity of hypoxia/anoxia in CB (Taft et al., 1980). Runoff may have increased with the clearance of land that began with early settlement in the 17th century and reached a maximum in the mid- to late 1800s (Cooper and Brush, 1991). Increased nutrient loading to CB began in the late 19th century with the increased use of natural phosphorus-based fertilizers (Wines, 1985), but increased dramatically with the introduction of industrially manufactured nitrogenous fertilizers in the early 20th century (Cornwell et al., 1996). Because of the temporal separation of these events, a precise chronology of the occurrence of anoxia and eutrophication in CB may lead to a better understanding of their ultimate cause.

In previous studies, Cooper and Brush (1991; 1993) used sedimentary indicators such as diatom population structure, TOC and sulfur concentration and degree of pyritization (DOP) to establish the occurrence of major environmental changes since European settlement in the CB watershed. However, this study did not have the temporal resolution necessary to establish a detailed chronology for the preceding century of increasing anthropogenic influence. Cornwell et al. (1996) examined the nutrient chemistry of sediments deposited during this century from the mesohaline region of the CB, but were unable to follow the history of eutrophication in the Bay due to post-depositional changes in elemental concentrations. In the present study, we analyze organic and inorganic geochemical indicators in sediments sampled at time intervals so as to establish a detailed chronology of the onset and history of eutrophication and anoxia in the mesohaline region of CB.

A further objective of this study was to examine how OM composition may have changed in response to eutrophication and anoxia. Researchers have noted increases in the concentration of TOC preserved in sediments of CB (Cooper and Brush, 1991, 1993; Cornwell and Sampou, 1995; Cornwell et al., 1996) and estuarine and coastal environments in general (e.g., Eadie et al., 1994; Gong and Hollander, 1997; Louchouarn et al., 1997) during the 20th century; but it is difficult to distinguish the effects of OM decomposition from those due to an increase in OM delivery to the sediments over time because both processes may yield the same downcore OM profile. In this study, diagenetic modeling and an examination of lipid biomarker distributions are used to distinguish between these possibilities as well as to elucidate the changing nature of OM deposited during this century of increasing anthropogenic influence. Lipids are useful geochemical tools in paleo-environmental reconstructions because of their low reactivity (high preservation potential) and source specificity relative to other organic compound classes (Cranwell, 1982; Brassell and Eglinton, 1986). Sedimentary distributions of fatty acid and sterol compounds were analyzed because compounds within these two lipid classes can be related to specific contributors of OM to CB sediments.

2. Materials and methods

2.1. Study site and sample collection

A 2.6-m sediment core was collected from the mainstem mesohaline region of the CB just south of the mouth of Choptank River (Site M3: 38°34.05′N;

76°26.76′ W), in 15 m of water (Fig. 1) during March of 1996. Sediments deposited here are likely to be representative of the mid-Bay region due to the high frequency tidal and meteorological turbulent mixing processes of this region of the Bay (Boicourt, 1992). Site M3 is located downstream (southward) of the turbidity maximum and immediately upstream of the location where peak spring bloom biomass typically occurs (Harding et al., 1986; Malone, 1992). After sinking, OM from points southward may also be advected by north-flowing bottom waters to the mid-Bay (Malone, 1992) where decomposition and deposition may occur. For these reasons, seasonal anoxia/hypoxia is most commonly observed, and oxygen depletion is most severe, in the mesohaline portion of the Bay (Taft et al., 1980; Officer et al., 1984a; Boicourt, 1992) and is likely to have first occurred at this site. Cornwell et al. (1996) have noted sediment accumulation rates at M3 high enough to obtain stratigraphic resolution sufficient for the construction of a detailed depositional history for the previous two centuries.

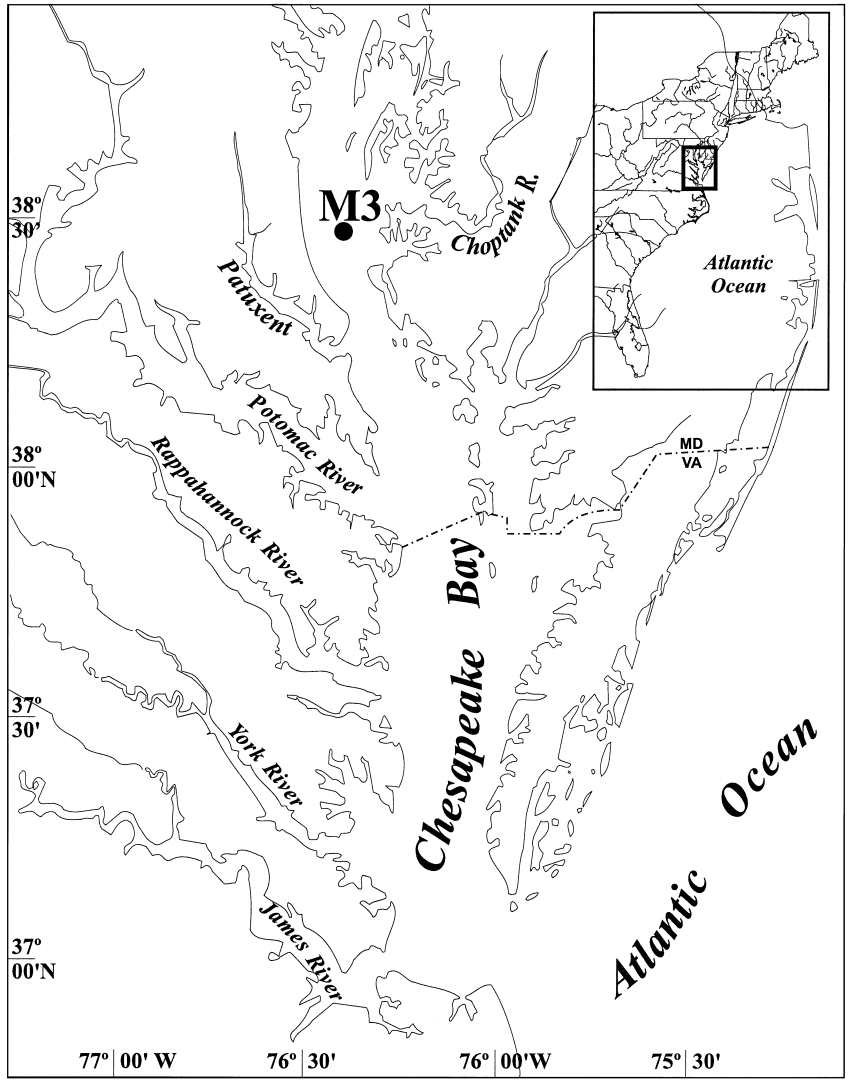

Fig. 1. Location of core collection site (M3) in the mesohaline portion of CB.

The core was collected using a large cross-section kasten corer (13 cm × 13 cm; Kuehl et al., 1986b) in order to minimize physical disturbance of the sediment during coring. Disruption of the core during handling was further reduced by the ability to remove one side of the core barrel, thus, eliminating disruption and compaction caused by core extrusion. The kasten core and an adjoining box core (26 cm depth) were subsampled at 0.5-cm intervals in the upper 5 cm of sediment. Subsamples consisting of 2-cm sections were collected at 5-cm intervals in the upper meter of the core and at 10-cm intervals in the remaining 1.6 m of the core. Subsamples were then homogenized and portions were placed in pre-combusted (450°C, 4.5 h) glass jars for organic and inorganic geochemical analyses and plastic centrifuge tubes for radioisotopic analysis. The core was subsampled and samples were frozen (−80°C for organic analyses, −20°C for inorganic analyses) within 24 h of core collection.

2.2. Analytical methods

Sediments were dated using ^{210}Pb and ^{137}Cs radiochronology in combination with pollen and microfossil stratigraphy. ^{210}Pb activity was measured by alpha spectrometric methods with a ^{209}Po spike serving as a yield determinant according to the methods of Nittrouer et al. (1979) and Kuehl et al. (1986a). Additional dating information was provided by pollen analysis using the methods of Willard (1994) and correlated with microfossil stratigraphy, both carried out at USGS-Reston by Drs. D. Willard and T. Cronin. Sediments were analyzed for TOC and total nitrogen (TN) following the methods of Hedges and Stern (1979) in which dried sediments are acidified with HCl to remove carbonate prior to analysis by a Carlo Erba Elemental Analyzer 1108. Biogenic silica (BSi) analysis by a series of extractions into Na_2CO_3, and sulfur speciation analysis by acidification to H_2S followed by Pb-titration were carried out according to the methods of DeMaster (1981) and Cornwell and Morse (1987), respectively. Detailed description of the organic geochemical methods employed may be found in Canuel and Martens (1993). Briefly, lipids were extracted from wet sediments into chloroform/methanol (2:1, v/v) aided by sonication. Following saponification, fatty acids were converted to methyl esters. Fatty acid methyl esters and sterols/alcohols were separated from other lipid compound classes by silica gel chromatography. Sterols were derivatized to TMS-ethers and both fractions were analyzed by gas chromatography. Compound concentrations were quantified by comparison of peak area to that of an internal standard compound (C_{21} fatty acid methyl ester or 5α-cholestane) added prior to GC analysis. Final concentrations were adjusted to account for varying sample-to-sample extraction efficiency that was determined by percentage recovery of standard compounds (C_{20} fatty acid–C_{14} alcohol ester) added prior to extraction. Peak identifications were confirmed using gas chromatography-mass spectrometry.

3. Results

3.1. Sediment dating

Excess ^{210}Pb activity was present in the sediments of the M3 core from the surface to almost 100 cm true depth (Fig. 2a). Plotted on a logarithmic scale, the strong linear relationship between excess activity and depth ($r^2 = 0.951$; $p < 0.001$) indicates no evidence of physical or biological disturbance and a constant sediment mass accumulation rate of 0.477 g cm^{-2} yr^{-1} was calculated. This sediment accumulation rate is within the range of values published for this region of the Bay (Officer et al., 1984b; Cornwell et al., 1996). X-ray radiographs of sections of the core (0–30, 37–67, 140–170 cm true depth: viewable at www.vims.edu/~azimmer) displayed fine laminae and few tube burrows, also indicating little disturbance to the sediment. Matching radioisotope activities at similar depths in the box and kasten core provide evidence that the surficial sediments were well recovered by the kasten core. To correct for differential compaction of the core, depth was normalized to the mean porosity of 0.89 (calculated by drying and reweighing sediments to obtain water content and then correcting for pore water salt content and assuming an average sediment density of 2.6 g cm^{-3}). A linear accumulation rate of 1.67 cm yr^{-1} was then calculated. It is important to note that, while the choice of normalization porosity will affect the linear accumulation rate, it will not influence the

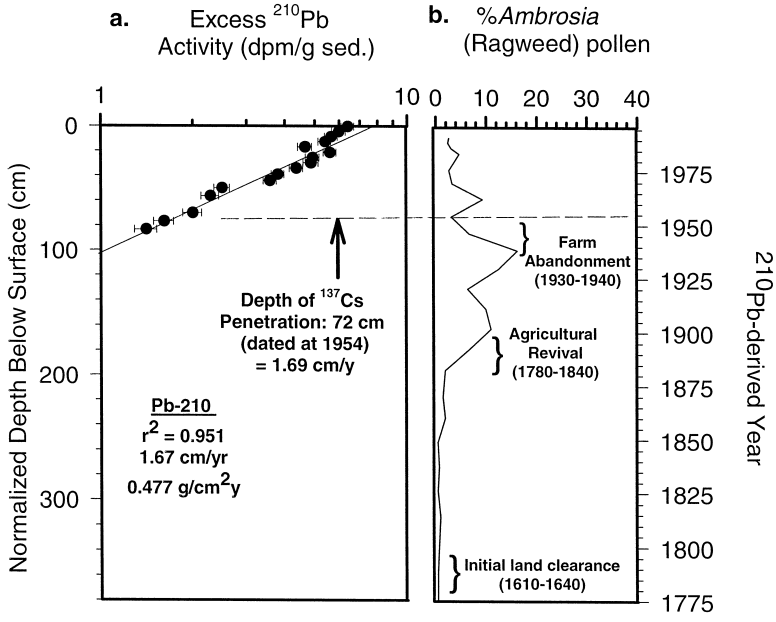

Fig. 2. Dating of M3 core using (a) ^{210}Pb and ^{137}Cs radiochronology and (b) ragweed pollen (%) with date assignments. Depth, on left is normalized to a mean porosity of 0.89 and correlate to dates (at right) based on the ^{210}Pb-derived constant accumulation rate.

calculated mass accumulation rate. Likewise, the date assignments of individual samples will not be affected because their relative normalized depth is unchanged by the choice of normalization porosity. Only normalized depth is referred to hereafter, but both are listed in Table 1 for the purpose of conversion. ^{137}Cs was present in the core to a depth of 70 cm. By assuming 1954 as the year of initial input (Ritchie and McHenrey, 1990), a linear accumulation rate of 1.69 cm yr^{-1} is calculated. Maximum ^{137}Cs activity was measured in a sample at 55 cm depth in the core. Using 1964 as the accepted year of maximum input (Ritchie and McHenrey, 1990), an accumulation rate of 1.70 cm yr^{-1} is calculated. Both ^{137}Cs-derived accumulation rates are in close agreement with the ^{210}Pb-derived rate.

It would be inappropriate to assume that the ^{210}Pb-derived accumulation rate can be extended below 100 cm depth (the 'lower' core) where there is no excess ^{210}Pb activity considering evidence (Brush, 1989; Cooper and Brush, 1991) that accumulation rates have increased during the past three centuries at some sites in CB due to agricultural development in the watershed. We have, instead, used dated pollen horizons to provide age estimates for discrete sediment horizons in the lower portion of the core (Fig. 2b). For example, clearance of land during the initial phase of European settlement occurred between 1610 and 1640 in this region and is indicated in the sediment by an increase in the proportion of *Ambrosia* (ragweed) pollen (a change from $<1\%$ to $>1\%$) relative to other types of pollen (Brush, 1984; Brush et al., 1982). This horizon occurs between 388 cm (core bottom) and 324 cm depth in the core. The 'agricultural revival', or shift to intensive agricultural land usage (1780–1840), indicated by an increase in the relative proportion of ragweed to greater than 10% and a decrease in the oak/ragweed pollen ratio to less than 5% (Brush, 1984; Brush et al., 1982), is found between 190 and 150 cm depth in the core. Lastly, a decrease in the relative amount of ragweed pollen (95–80 cm depth) corresponds to the period of farm abandonment and forest regrowth which, although beginning in the mid-19th century, saw increased rates during the Depression of the 1930s (Brush, 1989). Together, pollen/microfossil indicators indicate an accumulation rate closer to 1.0 cm yr^{-1} for the lower (<100 cm depth) portion of the core (versus 1.67 cm yr^{-1} for the upper core). As it is

Table 1
Bulk geochemical characteristics of Site M3 kasten core

True depth interval (cm)	Normalized depth (cm)	^{210}Pb date[a] (year)	Organic C (mg C g^{-1} dry sediment)	Total N (mg N g^{-1} dry sediment)	AVS[b] (μmol g^{-1} dry sediment)	CRS[c] (μmol g^{-1} dry sediment)	AVS/CRS
0–0.5	0.09	1996.2	34.6	4.7	15.9	234.4	0.07
0.5–1.0	0.28	1996.1	36.5	5.3	23.8	218.6	0.11
1.0–1.5	0.57	1995.9	35.9	4.8	n.d.[d]	n.d.	n.d.
1.5–2.0	0.97	1995.7	34.1	4.5	41.2	171.7	0.24
2.0–2.5	1.36	1995.4	34.1	4.6	52.7	176.1	0.30
2.5–3.0	1.76	1995.2	33.8	4.5	39.7	193.6	0.20
3.0–3.5	2.16	1995.0	32.8	4.5	40.7	202.6	0.20
3.5–4.0	2.56	1994.7	32.7	4.6	73.4	167.3	0.44
4.0–4.5	2.95	1994.5	33.4	4.6	65.5	194.3	0.34
4.5–5.0	3.35	1994.2	32.8	4.5	62.0	204.8	0.30
5.0–7.0	4.34	1993.7	31.4	4.2	32.8	285.7	0.11
10–12	8.57	1991.1	27.2	3.5	39.3	225.1	0.17
15–17	12.62	1988.7	26.9	3.4	66.1	238.3	0.28
20–22	16.88	1986.1	29.1	3.6	37.0	247.0	0.15
25–27	21.28	1983.5	28.5	3.8	43.5	325.6	0.13
40–42	34.11	1975.8	26.4	3.3	29.2	241.0	0.12
50–52	44.36	1969.6	27.7	3.2	17.2	109.0	0.16
60–62	56.71	1962.2	25.8	2.8	16.7	108.6	0.15
62.5–63	59.05	1960.8	24.9	2.8	n.d.	n.d.	n.d.
63–63.5	59.72	1960.4	24.7	2.7	15.3	124.6	0.12
63.5–67	62.40	1958.8	24.1	2.7	14.7	100.8	0.15
70–72	70.11	1954.2	25.0	2.7	10.0	107.7	0.09
75–77	76.78	1950.2	26.0	2.7	14.6	95.8	0.15
80–82	83.36	1946.2	25.8	2.6	14.4	111.3	0.13
85–87	89.94	1942.3	24.9	2.5	6.4	126.9	0.05
90–92	96.69	1938.3	25.1	2.4	11.2	131.1	0.09
100–102	111.17	1929.6	19.0	2.2	6.0	402.3	0.01
110–112	126.51	1910	17.4	2.2	n.d.	n.d.	n.d.
120–122	141.92	1891	17.1	2.1	4.4	423.0	0.01
130–132	157.46	1872	17.4	2.2	3.5	365.2	0.01
150–152	189.61	1832	16.3	2.1	3.3	324.3	0.01
170–172	226.85	1785	15.2	1.9	1.6	327.1	0.00
190–192	264.18	1738	15.4	2.0	1.2	300.8	0.00
210–212	303.34	1689	16.0	1.9	1.7	322.0	0.01
240–242	366.88	1610	14.8	1.8	n.d.	n.d.	n.d.

[a]Ages below 110 cm are derived from pollen analysis.
[b]AVS = iron monosulfide (FeS).
[c]CRS = pyrite and elemental sulfur (FeS_2 and S^0).
[d]n.d. = not determined.

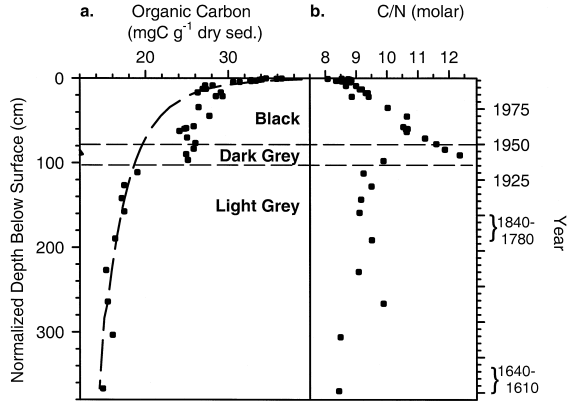

Fig. 3. (a) TOC concentration in site M3 sediments. Curve plotted is TOC calculated using the model of Middelburg (1989) assuming constant organic carbon accumulation. (b) Molar TOC/TN ratio. Dashed horizontal lines represent sediment color change horizons. Depth, on left is normalized to a mean porosity of 0.89 and correlate to dates (at right) based on the ^{210}Pb-derived constant accumulation rate since 1925 and pollen chronology prior to 1925.

difficult to model this gradual change in accumulation rate and most of the chemical changes occur in the upper portion of the core, we present the chemical stratigraphies based upon a constant linear accumulation rate of 1.67 cm yr^{-1} for the upper portion of the core, and indicate specific horizons that can be constrained in age by pollen stratigraphy in the lower core.

3.2. Bulk geochemistry

The sediment was marked by abrupt changes in color at two horizons: from light gray in the lower core to dark gray at 100 cm depth corresponding to the year 1934 ($\pm$5 years), and from dark gray to black in the upper portion of the core at 80 cm depth corresponding to the year 1948 ($\pm$4 years). These horizons are indicated by dashed lines on all of the following geochemical profiles and tables both for reference and because significant geochemical changes occur across these horizons. The concentration profiles of radiogenic isotopes and other geochemical variations cannot be attributed to grain size variation, which remains constant throughout the core (determined gravimetrically by differential settling).

TOC concentrations increase abruptly (by 40%) across the 1934 sediment horizon from an average concentration of 17.7 ($\pm$0.86) mg C g^{-1} sediment in the 40 cm below, to 25.1 ($\pm$0.61) mg C g^{-1} sediment in the 40 cm above this horizon (Fig. 3a and Table 1). In the upper 10 cm of the core, TOC concentrations rapidly increase to 34.6 mg C g^{-1} sediment at the sediment surface. The rate of upcore increase in TN concentration is more gradual and shows no abrupt transitions except for a slight increase above the 1934 horizon and a rapid increase in the upper 10 cm of the core (Table 1). As a result, the molar ratio of C/N also changes dramatically across the 1934 sediment horizon, increasing from 9.9 to 12.4 (Fig. 3b). C/N decreases from the 1934 horizon to the surface sediment to values between 8 and 9, typical of algal-derived OM sources (Meyers, 1994). The C/N decrease since 1934 could be due either to preferential remineralization of N relative to TOC over time or to increases in deposition of algal versus terrestrial OM. Also plotted in Fig. 3a, is an organic carbon profile predicted by the diagenetic model of Middelburg (1989), which assumes steady input and a time-dependent decomposition rate parameter. Between 1934 and 1986, there has been OM preservation in excess of that predicted by this diagenetic model. The nature and origin of this excess OM is investigated using diagenetic models, lipid biomarkers and other geochemical indicators (below).

Concentrations of biogenic silica (BSi; Fig. 4a) remain generally constant at depths below 100 cm

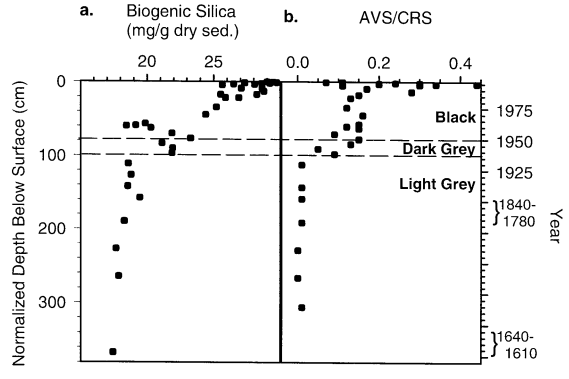

Fig. 4. (a) Biogenic silica (mg g^{-1} dry sediment), and (b) the ratio of acid volatile sulfur (AVS) to chromium reducible sulfur (CRS) in M3 core sediments. Vertical axes are as indicated in Fig. 3.

(mean = 17.9 ± 1.5 mg g^{-1} dry sediment). Across the 1934 sediment horizon, BSi increases by an average of 20% (mean of 21.6 ± 2.1 mg g^{-1} dry sediment dated between 1934 and 1970). Except for a single interval of lower BSi concentration (56–60 cm depth), sediment BSi concentrations generally increase from the 1934 horizon to the surface and average 28.1 ± 1.7 mg g^{-1} dry sediment in sediments deposited since 1970. BSi and TOC concentrations are linearly correlated throughout the core ($r^2 = 0.786$; $p < 0.001$).

The ratio of AVS (= FeS) to CRS (= pyrite and S^0) is an indicator of bottom water oxygenation conditions (Roden and Tuttle, 1993). Because sulfur as FeS is in a lower oxidation state than sulfur as pyrite, an increase in this ratio indicates a depositional environment lower in free oxygen. The AVS/CRS ratio provides a more reliable proxy for bottom water oxygenation condition than DOP because it is less affected by changes in Fe availability. Roden and Tuttle (1993) found higher AVS/CRS ratios in surface sediments of CB in areas of relatively stronger reducing conditions. In the M3 core, both CRS and AVS remain at a constant concentration in the lower (pre-1934) portion of the core (Table 1). CRS concentrations decrease abruptly (from 402 to 131 μmol g^{-1} dry sediment) across the 1934 sediment horizon, whereas AVS doubles. The sediment AVS/CRS ratio increases progressively in sediments deposited between 1934 and 1948 (Fig. 4b) indicating either a transition to stronger reducing conditions or to more frequent occurrences of hypoxic/anoxic conditions at the study site (Fig. 4b). The AVS/CRS ratio remains relatively constant between 1948 and 1986 (an order of magnitude higher than in pre-1934 sediments) and increases again in the top 5 cm. Total sulfur, as determined by elemental analyzer, also increases by 39% from the sample immediately below to above the 1934 sediment horizon (data not shown).

3.3. Lipid biomarkers

Total extractable lipid (determined gravimetrically) ranges from 47 mg g^{-1} dry sediment in the surface sediments to 3.6 mg g^{-1} dry sediment in the oldest sediments. Concentrations (μg g^{-1} dry sediment) of total sterols, total fatty acids and fatty acid compound classes, and selected neutral lipid (sterol, hopanol and fatty alcohol) compounds are presented in Table 2. Concentrations of selected fatty acid compounds used as biomarkers are shown in Table 3. The compounds listed and discussed in the following were chosen because unambiguous source assignments could be made for these compounds and they were present in large enough abundance to be reliably quantified. Note that both the 16.9 cm and the 366.9 cm depth sample were analyzed twice (the latter for neutral lipids only). While most duplicate analyses were within 20% agreement, some differed by a factor of two. However, all duplicate compound analyses were within a range necessary to validate the following trends.

Overall, the upper 2 cm of the core (three samples) have lipid compound and compound class abundances that greatly exceed the rest of the core. For example, most sterol and fatty acid compounds and compound classes are 2–4 times more abundant in the upper 2 cm of the core relative to the 4–17-cm interval. However, the hopanols and long-chain alcohols are only slightly enriched (1 to 1.5 times), whereas certain polyunsaturated and branched fatty acids, as a whole, were 4–15 times more abundant in the upper 2 cm of the core. Concentrations of all the compound and compound classes examined decrease downward in the core and tend to reach a level of constant concentration at depths ranging from 80 to 100 cm.

By expressing lipid concentrations relative to TOC, the effects of differential diagenetic decomposition on compound abundances over time are lessened, whereas the changing quality of the OM that has been preserved since 1934 is revealed. Individual lipid compounds derived from plankton (Fig. 5) and microbial sources (Fig. 6) show similar patterns of post-1948 enrichment relative to TOC, possibly signaling an increase in autotrophic and heterotrophic production in the mesohaline region of the Bay at that time. For example, OM deposited in the 30 years after 1948 is, on average, nearly twice as rich in 24-methylcholesta-5,22-dien-3β-ol (brassicasterol) and 24-methylcholesta-5,24(28)-dien-3β-ol (24-methylenecholesterol), both derived mainly from diatoms (Orcutt and Patterson, 1975; Kates et al., 1978; Berenberg and Patterson, 1981; Gillan et al., 1981; Volkman, 1986), relative to OM deposited

Table 2
Sterol and *n*-alcohol biomarker compound and lipid group concentrations (μg g^{-1} dry sediment) in Site M3 kasten core

Normalized depth (cm)	Lipid compound classes						Plankton biomarkers					Bacterial markers		Terrestrial markers	
	Total sterols	Total fatty acids	Total saturated fatty acids	Total mono-unsaturated fatty acids	Total poly-unsaturated fatty acids	Total branched fatty acids	24-Methyl-cholesta-5,22-dien-3β-ol (brassicasterol)	24-Methyl-cholesta-5,24(28)-dien-3β-ol	Cholest-5-en-3β-ol (cholesterol)	4α,23,24-Trimethyl-cholest-22-en-3β-ol (dinosterol)	4α,23,24-Trimethyl-5α(*H*)-cholestan-3β-ol	Hopan-3β-ol	Extended hopanol	C_{22} *n*-alcohol	C_{24} *n*-alcohol
0	175.12	558.45	302.17	180.50	19.01	56.76	16.72	23.48	23.92	15.56	3.06	1.26	2.24	2.62	2.49
0.6	148.51	179.52	71.31	70.41	22.47	15.34	5.64	3.12	15.08	4.40	1.15	0.32	3.14	1.83	1.46
1.8	139.22	231.43	136.20	58.42	4.91	31.90	9.07	7.27	13.27	14.75	3.53	1.55	5.05	2.32	2.12
4.3	68.26	95.27	45.88	36.67	6.98	5.73	2.19	1.63	2.91	2.03	2.74	0.92	2.15	0.91	0.89
12.6	117.10	194.99	96.43	65.63	23.37	9.56	3.52	5.28	6.06	3.25	4.31	1.87	3.79	2.05	2.05
16.9	66.50	71.79	45.13	16.34	2.50	7.82	4.24	2.48	3.88	10.62	2.25	0.75	3.36	1.86	1.70
16.9	53.22	79.67	44.76	22.79	4.89	7.23	3.39	2.19	2.90	8.07	1.80	0.64	2.66	1.59	1.36
25.6	99.33	130.81	65.49	42.85	15.51	6.95	2.83	2.26	4.15	2.42	4.31	0.94	4.50	1.81	1.85
34.1	51.93	47.60	33.34	7.17	2.26	4.82	3.31	1.95	2.76	7.16	1.85	0.55	2.55	1.67	1.59
44.4	49.26	38.55	26.55	6.14	1.25	4.12	3.12	1.74	2.34	4.38	1.11	1.83	2.81	0.28	0.17
50.2	72.67	41.78	21.02	12.77	4.54	3.45	2.11	1.67	3.38	1.87	3.30	0.79	4.02	1.85	1.28
56.7	44.78	29.66	23.97	2.77	1.59	1.33	3.04	1.95	2.27	5.77	1.14	1.35	2.12	1.85	1.63
59.7	28.20	36.75	26.78	6.30	0.55	3.12	1.70	1.29	1.24	4.20	1.36	0.80	1.66	1.54	1.20
62.4	34.30	38.85	27.51	6.30	0.38	4.16	2.39	1.48	1.76	3.31	1.21	1.42	2.61	0.25	0.13
70.1	30.65	63.19	28.54	19.13	14.17	1.35	0.80	0.62	1.20	0.94	1.69	0.38	1.43	0.97	0.90
76.8	32.51	21.04	14.62	3.17	1.59	1.66	2.06	1.64	1.56	4.87	1.35	0.69	1.75	1.93	1.42
83.4	32.32	35.78	23.84	6.22	2.34	3.37	1.76	1.49	1.44	4.48	1.22	1.06	2.09	1.72	1.31
89.9	20.66	18.84	10.54	4.82	2.90	0.59	0.59	0.63	0.98	0.53	1.25	0.49	1.05	0.82	0.81
96.7	24.26	17.75	11.49	3.31	0.80	1.85	1.78	1.26	1.46	2.41	0.66	0.85	1.35	0.22	0.09
111.2	18.70	23.13	17.93	2.94	0.15	1.73	1.14	0.73	0.83	2.68	0.80	0.76	0.97	1.38	1.12
126.5	15.97	6.12	4.10	1.56	0.33	0.12	0.43	0.32	0.67	0.49	1.05	0.22	0.68	0.61	0.76
141.9	18.66	21.64	16.13	2.80	0.28	1.84	0.98	0.93	0.95	2.62	0.62	0.87	0.76	1.35	1.35
157.5	21.68	25.86	16.16	7.92	0.75	0.93	0.54	0.51	0.87	0.60	1.46	0.34	0.87	0.83	1.11
189.6	18.47	20.71	16.00	2.44	0.31	1.75	0.94	0.83	0.89	2.40	0.81	0.89	1.07	0.95	1.01
226.9	19.02	24.53	13.48	6.95	2.51	1.58	0.54	0.32	1.40	0.33	1.83	0.54	0.81	1.19	1.56
283.4	13.18	12.21	6.73	2.70	1.84	0.94	0.50	0.30	1.14	0.16	0.04	0.48	0.74	0.99	1.35
366.9	12.55	11.54	7.72	1.92	0.78	0.76	0.82	0.60	1.02	0.84	0.17	0.79	0.53	0.03	1.57
366.9	15.22	n.d.	n.d.	n.d.	n.d.	n.d.	0.42	0.42	1.64	0.22	1.72	0.52	0.54	1.61	1.22

Table 3
Fatty acid biomarker compound concentrations (μg g^{-1} dry sediment) in Site M3 kasten core

Normalized depth (cm)	Plankton biomarkers										Bacterial biomarkers					Terrestrial biomarkers			
	MUFA[a]		C_{20} and C_{22} polyunsaturated fatty acids[a]								Branched fatty acids[b]					Long-chain saturated *n*-FAs			
	16:1 ω9	18:1 ω9	20:5	20:4	20:3	20:2	22:6	22:5	22:4	22:2	*i*15	*a*15	*i*17	*a*17	10Me16	C_{22}	C_{24}	C_{26}	C_{28}
0	112.89	27.38	2.28	3.64	2.86	2.23	0.00	1.06	1.23	0.00	2.86	18.50	5.53	5.50	8.37	4.98	6.18	11.53	1.01
0.6	2.62	16.66	1.86	3.02	0.63	0.86	1.50	2.03	10.44	0.00	0.61	4.40	1.47	2.95	2.74	1.44	1.45	1.32	0.00
1.8	16.21	11.64	0.46	0.00	0.65	1.42	0.00	0.00	0.00	0.00	1.29	9.08	3.74	4.07	5.14	3.73	4.54	3.07	0.81
4.3	5.69	14.92	0.26	0.26	0.63	0.47	0.00	4.99	0.00	0.00	0.00	1.06	0.52	1.13	1.05	0.61	0.66	0.52	0.00
12.6	6.24	28.95	0.44	0.98	0.53	0.82	0.00	0.00	0.00	19.16	0.31	1.23	0.88	1.84	0.89	1.33	1.68	2.28	0.37
16.9	3.98	4.35	0.00	0.00	0.00	0.00	0.00	0.00	2.50	0.00	0.00	1.90	1.03	1.58	1.84	0.00	3.28	2.57	0.90
16.9	9.38	4.47	0.72	0.98	0.55	0.40	0.00	0.55	0.00	0.00	0.00	1.69	0.91	1.36	1.76	2.18	2.95	2.11	0.84
25.6	1.89	19.52	0.28	0.51	0.00	0.40	0.00	0.00	0.00	12.09	0.28	0.88	0.64	1.44	0.51	1.02	1.41	2.07	0.83
34.1	1.77	2.99	0.00	0.00	0.00	0.00	0.00	0.00	0.00	2.26	0.00	1.20	0.63	0.96	0.97	0.00	3.51	1.92	0.97
44.4	1.46	2.10	0.23	0.18	0.24	0.00	0.00	0.16	0.25	0.19	0.40	0.96	0.48	0.82	0.59	1.74	2.70	2.32	0.79
50.2	3.47	4.16	0.40	0.00	0.00	0.00	0.00	0.00	3.22	0.00	0.00	0.66	0.37	0.58	0.56	0.82	1.08	0.43	0.00
56.7	0.60	1.26	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.59	0.00	0.62	0.00	0.71	0.00	0.00	2.26	2.57	0.64
59.7	1.57	2.30	0.00	0.00	0.22	0.16	0.00	0.17	0.00	0.00	0.00	0.77	0.47	0.69	0.45	1.71	2.49	2.09	0.83
62.4	1.61	2.17	0.00	0.00	0.00	0.00	0.00	0.00	0.18	0.20	0.39	0.94	0.49	0.87	0.61	1.71	2.82	2.05	0.88
70.1	1.09	8.48	0.00	0.28	0.00	0.24	6.59	0.00	0.00	6.54	0.00	0.24	0.00	0.21	0.00	0.39	0.58	1.04	0.76
76.8	0.84	1.23	0.00	0.00	0.00	0.13	0.00	0.00	0.00	1.46	0.00	0.46	0.00	0.41	0.32	0.00	1.69	0.91	0.48
83.4	1.68	2.55	0.25	0.17	0.00	0.00	0.41	0.68	0.18	0.16	0.33	0.75	0.41	0.70	0.43	1.64	2.21	1.68	0.68
89.9	0.37	2.14	0.00	0.00	0.14	0.14	0.00	2.44	0.00	0.00	0.00	0.15	0.00	0.12	0.00	0.32	0.48	0.29	0.10
96.7	0.64	1.30	0.00	0.08	0.08	0.06	0.00	0.00	0.00	0.38	0.18	0.39	0.22	0.32	0.17	0.83	1.32	1.11	0.49
111.2	0.62	1.09	0.00	0.15	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.50	0.27	0.46	0.00	1.39	2.00	1.51	0.83
126.5	0.25	0.67	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.33	0.00	0.12	0.00	0.00	0.00	0.18	0.23	0.10	0.00
141.9	0.69	0.87	0.00	0.00	0.00	0.18	0.00	0.00	0.00	0.10	0.24	0.49	0.25	0.41	0.00	1.60	1.72	1.40	0.91
157.5	0.37	4.13	0.13	0.10	0.14	0.27	0.00	0.00	0.00	0.00	0.12	0.20	0.00	0.11	0.00	2.72	0.37	0.39	0.00
189.6	0.43	0.70	0.15	0.00	0.00	0.00	0.00	0.00	0.09	0.07	0.19	0.42	0.20	0.33	0.17	1.86	1.98	1.92	0.93
226.9	0.52	2.77	0.13	0.08	0.12	0.15	0.09	0.00	1.34	0.00	0.11	0.23	0.09	0.14	0.10	0.73	0.60	0.21	0.13
283.4	0.24	1.19	0.04	0.08	0.05	0.08	0.00	0.00	1.34	0.00	0.06	0.14	0.05	0.08	0.06	0.48	0.45	0.09	0.09
366.9	0.20	0.34	0.07	0.00	0.06	0.03	0.13	0.08	0.00	0.18	0.11	0.23	0.11	0.16	0.09	0.91	0.91	0.90	0.44

[a] Monounsaturated (MUFA) and polyunsaturated fatty (PUFA) acids: *A*:*B*ω*C* designation where *A* is the number of carbon atoms, *B* is the number of double bonds, and *C* (when known) is the double bond position from the aliphatic (ω) end of the molecule.

[b] *i* = *iso*, in which the branched methyl group on the fatty acid is at the ω − 1 position. *a* = *anteiso*, in which the methyl group is at the ω − 2 position. 10Me16 methyl group branched at the ω − 10 position.

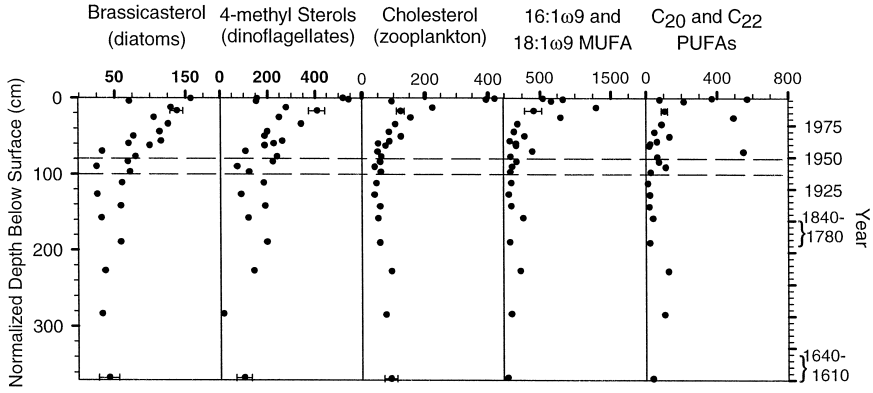

Fig. 5. TOC normalized concentrations (ng mg^{-1} TOC) of lipid biomarkers derived from planktonic sources in sediments of M3 core. Error bars represent the range of duplicate analyses of a single sample. Vertical axes are as indicated in Fig. 3.

prior to 1934. These enrichments increase progressively to the present. The influence of diagenesis on these geochemical profiles will be examined further in Section 4. The 4-methyl sterols, derived mainly from dinoflagellates (Boon et al., 1979; Volkman, 1986), display a similar pattern of progressive enrichment (65% increase in the 30 years after 1948 relative to before 1934). Other lipid biomarkers with mixed planktonic sources including 16:1ω9 and 18:1ω9 monounsaturated fatty acids, and C_{20} and C_{22} polyunsaturated fatty acids primarily derived from phytoplankton (Cranwell, 1982; Volkman, 1986; Killops and Killops, 1993), as well as cholest-5-en-3β-ol (cholesterol), mainly from zooplankton (Volkman, 1986; Killops and Killops, 1993), are enriched relative to carbon by 57%, 177% and 25%, respectively, during the same time period.

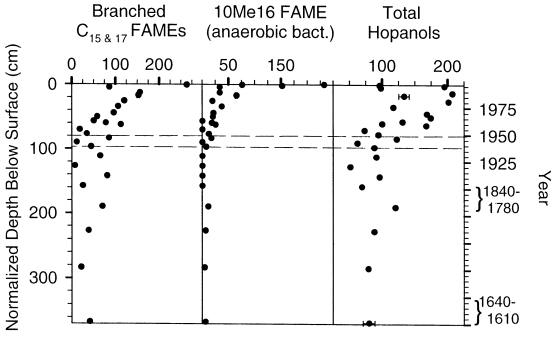

Fig. 6. TOC normalized concentrations (ng mg^{-1} TOC) of lipid biomarkers from microbially derived sources in sediments of M3 core. Error bars represent the range of duplicate analyses of a single sample. Vertical axes are as indicated in Fig. 3.

Lipid compounds typically derived from bacterial sources such as the *iso*- and *anteiso*-branched C_{15} and C_{17} and 10-methyl 16:0 fatty acids, characteristic of sulfate-reducing bacteria (Parkes and Taylor, 1983; Edlund et al., 1985; Kaneda, 1991) and the hopanols derived from a variety of bacteria (Ourisson et al., 1979; Cranwell, 1982; Rohmer et al., 1984) and some bactivorous ciliates (Harvey and McManus, 1991) are similarly enriched in the upper portion of the core (Fig. 6). Relative to TOC, sediments deposited between 1948 and 1970 are more enriched in these three microbially derived lipid groups than older sediments (by 57%, 46% and 314%, respectively). Note that while concentrations of these biomarker compounds are variable in bacteria, the source-specificity of these compounds still allows for their use as conservative indicators of relative changes in OM contributions from microbial sources. Phospholipid fatty acid data (unpublished) indicate that 5%–15% of the sedimentary fatty acids may be present as viable bacterial biomass. This proportion is closer to 30% in near-surface sediments and for branched fatty acids in particular. It is also unclear at present, what portion of the bacterial signal may be derived from sedimentary versus water-column bacterial communities.

In contrast, the amount of OM likely to have been derived from terrestrial sources shows no overall enrichment since 1948 (Fig. 7). TOC-normalized concentrations of total long-chain even-numbered

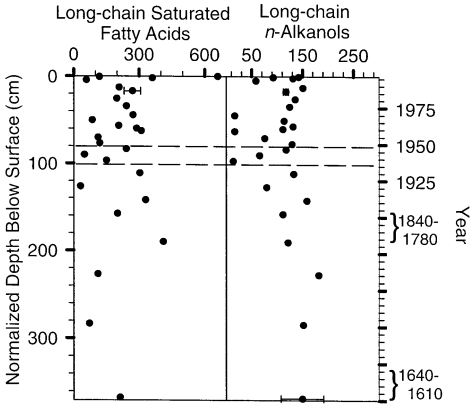

Fig. 7. TOC normalized concentrations (ng mg^{-1} TOC) of lipid biomarkers from terrestrially derived sources in sediments of M3 core. Error bars represent the range of duplicate analyses of a single sample. Vertical axes are as indicated in Fig. 3.

n-alkanoic acids and *n*-alkanols, both derived from land-plants (Cranwell, 1982; Rieley et al., 1991), decrease by 5% and 36%, respectively, across this sediment horizon. The decrease may be attributable to increased deposition of autochthonous OM, while allochthonous OM deposition remains constant. Moreover, there is no significant difference in the concentrations of the terrestrially derived lipid compounds examined after versus prior to 1948 when expressed on a weight basis (Tables 2 and 3). The high degree of variability in the concentration of these compound in adjacent sediment horizons from each section of the core probably reflect inter-annual and seasonal variability in autochthonous material supply.

Three sterols that are often found in vascular plants, 24-ethylcholesta-5,22*E*-dien-3β-ol (stigmasterol), 24-methylcholest-5-en-3β-ol (campesterol), and 24-ethylcholest-5-en-3β-ol (β-sitosterol) (Nichols et al., 1982; Killops and Killops, 1993) were not used as biomarkers for terrestrial OM input to CB for two reasons. First, the source assignment of these markers cannot be said to be unambiguous as a number of studies have found significant quantities of these sterols in phytoplankton (Volkman, 1986; Volkman et al., 1981). Second, we have found that these compounds are often enriched in CB surface sediments underlying high productivity regions (mid-Bay) compared to northern-Bay surface sediments where one would expect terrestrially derived OM to be relatively more important (unpublished data). Coprostanol (5β-cholestan-3β-ol), a sterol derived from sewage input (Kanazawa and Teshima, 1978), was not found to be present in this core or any surface sediment samples from CB mainstem we have examined.

4. Discussion

4.1. History of anoxia / hypoxia

Our data suggest that a major environmental change in the mesohaline region of CB occurred between 1934 and 1948. We interpret the increased storage of AVS occurring at this time as an indication of a shift toward more reducing conditions in bottom waters. A concomitant decrease in CRS storage may be interpreted as sulfur loss due to dissolved sulfide release into anoxic bottom waters, a process that is observed today in CB (Millero, 1991; Roden and Tuttle, 1992). Other possibilities that could explain the decrease in total reduced sulfur include changes in iron availability and decreased sulfate reduction due either to decreased OM or sulfate supply. However, no significant change in reactive iron concentration was found throughout the sediments of the core (extracted with 1N HCl over 24 h at room temperature and measured by atomic absorption spectrophotometry). OM availability has obviously increased rather than decreased and climate and microfossil evidence indicate no unidirectional change in salinity of the Bay's bottom waters since the 1930s (Cronin et al., in press).

The stability of the AVS/CRS ratio between 1934 and 1983 may reflect the relatively consistent (or only slightly increasing) levels of seasonal anoxia present in the Bay during this time period (Seliger et al., 1985). Higher ratios in sediments deposited in the mid- to late 1980s reflect episodes of more severe anoxia characteristic of recent decades (Seliger and Boggs, 1988). Changes in sulfur speciation in the upper 4-cm portion of the core are probably related to active sulfate reduction and seasonal variability (Roden and Tuttle, 1993), so fine-scale interpretation of this region of the sediment is probably unwarranted. Cooper and Brush (1991; 1993) also

noted major increases in sedimentary DOP values as well as total sulfur occurring in the mid-20th century in cores from the same region. In contrast to this previous work, we see no evidence for progressive environmental degradation prior to 1934. In the sediments of a core from a nearby site, Cornwell and Sampou (1995) also observed a trend of increasing AVS from mid-century (1950) to the present, further suggesting that low-oxygen events may have increased in frequency or duration since that time in this region of the Bay.

Microfossil evidence further supports the conclusion that a major environmental change occurred during the 1930–1940s. The ratio of *Ammonia parkinsoniana* (a low-oxygen tolerant benthic foraminifera species) to *Elphidia excavatum* (an oxygen-sensitive foraminifera) has been used as an indicator of oxygen depletion in coastal environments (Sen Gupta et al., 1996). An examination of the benthic foraminiferal record of the M3 core (using the same samples that were analyzed in this study) along with other cores from the same region of the Bay found a major decrease in the abundance of *E. excavatum* and progressive increases in *A. parkinsoniana* across the 1934 sediment horizon (Karlsen et al., in press). Cooper and Brush (1993) and Cooper (1995) examined the diatom record in cores collected in the same region of CB. They found a dramatic increase in the centric/pennate diatom ratio and a decrease in diatom diversity, indicators of deteriorating water quality, in sediments deposited since 1940. However, these investigators also found shifts in these proxies beginning as early as the 18th century rather than the abrupt mid-20th century transition that we observe.

There may also be evidence for the onset of anoxia/hypoxia in this region of the Bay in the abrupt increase in carbon preservation that occurs at the 1934 sediment horizon. The factors that cause enhanced OM preservation are still controversial. While some have found evidence that oxygen depletion in bottom waters alone can lead to enhanced sedimentary organic carbon preservation, others argue that increased sediment accumulation rate is required to enhance TOC burial efficiency and, therefore, preservation (reviews in Henrichs, 1992 and Hedges and Keil, 1995). In the M3 core, sediment grain size and extent of bioturbation do not change across the 1934 horizon. Sediment accumulation rates may have increased by two-thirds over the last three centuries, but this change probably occurred gradually as radionuclide, pollen and microfossil data do not point to any abrupt change in sediment accumulation rate during this century that could lead to a sudden increase in TOC preservation. Two non-exclusive possibilities that might explain the TOC increase are: a sudden increase in water column productivity and subsequent OM delivery to the sediment, or a sudden onset of strengthened seasonal oxygen depletion resulting in less degradation of particulate OM in the water column or surficial sediment prior to burial. The abrupt transition may be linked, ultimately, to both climatological and anthropogenic causes. For example, the early 1930s were relatively dry, even drought years, while stream discharge for the Susquehanna and other Chesapeake tributaries were above average in the late 1930s and early 1940s (USGS). In addition to strengthened vertical stratification that isolates bottom waters from oxygen resupply, increased runoff probably carried with it nutrients derived from fertilizers that were applied at ever increasing rates in the 1930s (U.S. Bureau of the Census, 1975). The sudden onset of seasonal anoxia/hypoxia, therefore, may have been due to a simultaneous decrease in oxygen supply by advection and an increase in oxygen consumption by microbial mineralization of an increased amount of labile OM in the water column. In Section 4.2, TOC and organic biomarker concentration profiles are used to examine the evidence for advancing eutrophication (i.e., increased water column OM production) and changes in the character of OM deposited since 1934.

4.2. Temporal changes in OM composition and diagenesis

Biogenic silica, TOC and lipid biomarkers indicative of autochthonous sources increase on both a mass- and carbon-normalized basis in sediments deposited only after 1934. The problem we face, however, is resolving whether the TOC and lipid biomarker compound concentration profiles are produced by steady-state diagenetic processes or non-steady-state (increasing) inputs. That is, can the

downcore TOC profiles be predicted assuming OM input to the sediment surface has remained constant over the last century or must we posit some change in the amount or quality of OM deposited at this site? In the following discussion, we will assume that the constant mass accumulation rate that was calculated radiochronometrically applies to the whole core and, therefore, use concentrations of organic components in the sediment as indicators of influx and/or removal (degradation).

4.2.1. Total organic carbon

The degradation of sedimentary OM is often modeled using the first-order *G*-model (Berner, 1964) in which metabolizable OM (G_m) is assumed to be remineralized at a constant rate, k, at any time t, such that:

$$G_m = G_{m_o} e^{-kt} + G_\infty \quad (1)$$

where G_{m_o} represents the concentration of metabolizable TOC present at the sediment surface and G_∞ is the asymptotic TOC concentration at depth and represents non-metabolizable carbon. Note that k is an 'apparent' degradation rate constant that represents the sum of both OM removal (such as microbially mediated remineralization and geopolymerization or incorporation into a bound pool) and additive (such as microbial synthesis) diagenetic processes. Although the M3 core TOC profile can be fit to an exponential function (Fig. 8a, i.e., Eq. (1); the single *G*-model; $r^2 = 0.893$, $p < 0.0001$), there is structure in the pattern of residuals (observed values minus predicted values) that are suggestive of non-steady-state processes influencing TOC deposition or preservation particularly between 10 and 60 years before the present.

The multi-*G* model (Berner, 1980) incorporates the concept of distinct portions of the OM (G_1, $G_2, \ldots$, etc.), each with differing reactivities (k_1, $k_2, \ldots$, etc.). By converting Eq. (1) to its linear form:

$$\ln(G_t/G_{m_o}) = -kt + \ln(G_\infty/G_{m_o}) \quad (2)$$

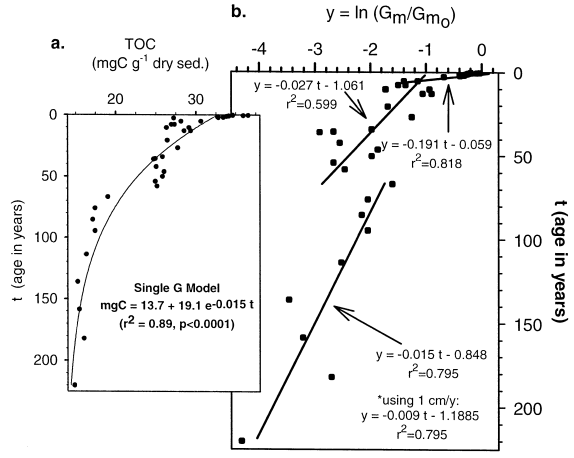

Fig. 8. (a) TOC concentration versus time and fit of simple exponential curve. (b) Plot of $\ln(G_m/G_{m_o})$ versus time. G_∞ was set at 24.0 mg C g^{-1} sediment for the upper (above 100 cm depth) portion of the core and 14.5 mg C g^{-1} sediment for G_∞ in the lower (below 100 cm depth) core. G_m values are the difference between measured TOC and G_∞. Linear relationships are shown for the time intervals: 0–3, 5–60 and 60–220 years ($p < 0.001$).

and plotting $\ln(G_t/G_{m_o})$ versus t, time periods of constant degradation rate (k = the slope) can be identified (Westrich and Berner, 1984). In the M3 core, it is apparent that there are three distinct portions of the TOC profile (Fig. 8b). The upper 10 cm of the profile (samples between 0.2 and 6 years in age) degrade with an apparent rate constant close to $-0.19\ yr^{-1}$. While it is difficult to compare systems for which environmental factors and OM composition may differ, this rate constant is of the same order of magnitude as those derived from both laboratory experiments and field observations of steady-state systems, where TOC decomposition was examined over time scales of days to a few years (Henrichs, 1992 and references therein). So, this portion of the TOC profile can be explained by a simple diagenetic model without invoking non-steady-state diagenetic processes. Modeled decay constants generally in the range of -0.03 to $-0.009\ yr^{-1}$ have been reported for TOC decomposition in sediments examined at time scales in the 10's to 100's of years range (Henrichs, 1992 and references therein). These rates are similar to the k of -0.027

and $-0.015\ yr^{-1}$ ($-0.009\ yr^{-1}$ using an accumulation rate of 1 cm yr^{-1}) for the 2–60 and 60–300 year-portion of the core, respectively. Direct comparison is difficult, however, because no other studies were found where OM degradation was examined at these time scales with similar sedimentation rates and OM quantity. It is of note, however, that a distinct increase (about $2\times$) in apparent k occurs at 60 years (100 cm depth). This could result from an increase in the lability of OM deposited since 1934, a progressively increasing quantity of OM deposited since 1934, or as an artifact of the graphical analysis (pointed out by Middelburg, 1989), or some combination of these explanations. In any case, despite the appearance of steady-state conditions within each of the three zones of the TOC profile, deposition and/or preservation conditions during the whole time period encompassed by this core can be characterized as non-steady state.

Another modeling approach is that of Middelburg (1989), who found that a strong relationship exists between the decay constant and time, reflecting a continuous decrease in the reactivity of OM with time since burial. A time-dependent rate parameter:

$$k = 0.16\ t^{-0.95} \quad (3)$$

was derived by Middelburg (1989) using both laboratory and field data, from both oxic and anoxic systems, and was shown to be valid over eight orders of magnitude of time. We find that this model under-predicts TOC preservation only in the 10–100 cm interval of the core (Fig. 3a). Further, k derived for time intervals (i.e., Δt between each sample) in the 0–10 cm and 100–400-cm portions of the core followed the relationship with time predicted by Eq. (3), while calculated k's in the 10–100 cm interval were greater than predicted. Non-steady-state conditions are suggested by the mismatch in the middle portion of the core (1934–1992). These observations suggest, but do not prove, the onset of eutrophication (i.e., increased OM input) in this region of the Bay beginning in 1934.

4.2.2. Lipid biomarkers

The profiles of the sterol, alcohol, and fatty acid biomarkers all show that the OM preserved in sediments deposited since 1934 is increasingly enriched in plankton and microbially derived material. By normalizing biomarker concentrations to TOC (Figs. 5–7), we have tried to eliminate some of the effects attributable to decomposition. However, a compound that decays at a rate greater than TOC will still appear to decrease in abundance downcore relative to TOC while a compound that decays at a rate less than that of TOC will appear to increase downcore. It has been shown that, at least at some time scales and in some environments, specific lipid biomarker compounds or compound groups decay at rates different from TOC and different from each other. Generally speaking, fatty acids are more reactive than TOC or sterols and increase in reactivity with increasing numbers of double bonds (Lee et al., 1977; Haddad et al., 1991; Sun and Wakeham, 1994; Sun et al., 1997; Canuel and Martens, 1996). It has also been shown that 4-methyl sterol compounds such as dinosterol are degraded at slower rates than cholesterol (Harvey et al., 1989; McCaffrey, 1990; Kennedy and Brassel, 1991; Sun and Wakeham, 1994). By examining the downcore ratio of some of these differentially reactive pairs, we can determine whether the biomarker record is likely to have been skewed by the effects of diagenesis. In the M3 core, the relative amounts of saturated, monounsaturated, polyunsaturated and branched fatty acids remains fairly constant below a core depth of 10 cm (Fig. 9). The same is true of cholesterol relative to dinosterol and the sum of fatty acid compounds relative to the sum of sterol compounds. Thus, the extent of remineralization/preservation of these lipid classes (in both the water column or sediment) has remained unchanged over the time period represented.

Published apparent rate constants for lipid decomposition also support the conclusion that the lipid profiles below 10 cm depth are not a result of diagenetic processes in this core. For example, in the Peru upwelling area, where accumulation rates are similar to that of the mesohaline CB, sterol decay constants were calculated to be in the range of 0.15 yr^{-1} for dinosterol to 0.54 yr^{-1} for cholesterol (McCaffrey, 1990). At these rates, 90% of the original compound abundance is removed after 20 and 5 years, respectively. Similarly, fatty acid and sterol degradation rate at Cape Lookout Bight, NC, where accumulation rates are 10 cm yr^{-1}, are such that

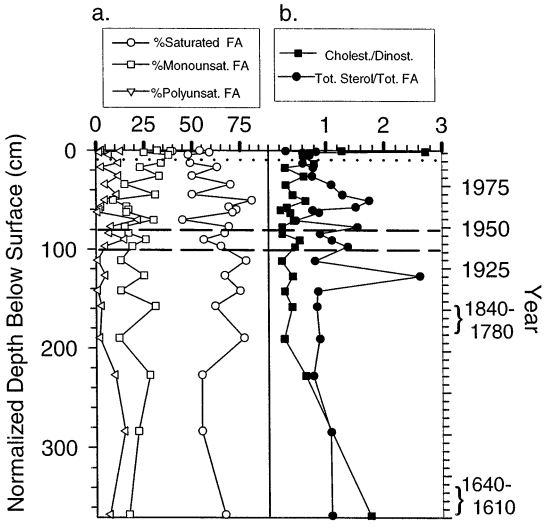

Fig. 9. (a) Downcore percentage abundance of saturated, monounsaturated and polyunsaturated fatty acids and (b) the ratio of cholesterol to dinosterol and total fatty acids to total sterols in M3 core sediments. Dotted line at 10 cm depth indicates the upper sediment zone of active diagenesis in this and the following figure.

90% of the diagenetic decrease would take place within 10–20 years of burial (Haddad et al., 1991; Canuel and Martens, 1996). The same cannot be said for lipids in Black Sea sediments where degradation constants were lower by at least an order of magnitude and asymptotic concentrations are not reached until at least 50 years of burial (Sun and Wakeham, 1994). This system may not be comparable, however, in that accumulation rates are much lower (< 0.02 cm yr^{-1}) and TOC concentrations are twice that of the M3 core.

The preponderance of evidence indicates that the supply of autochthonous OM to the study site has increased since 1934. Without evidence for a change in preservation conditions, we must choose non-steady-state input (increased input) to explain the 2-fold (3-fold if the lower accumulation rate supported by pollen dates is used) increase in apparent k that characterize sediments deposited after 1934. It would be highly improbable that, in this system, decomposition rates of the lipid biomarker compounds examined were all the same such that asymptotic concentrations are reached after 60 years of burial. Instead, it appears that the various sources of these biomarker compounds such as dinoflagellates for dinosterol and mainly zooplankton for cholesterol have recorded synchronously increasing OM contributions to the sediment. It is a matter of concern, whether organic biomarker proxies for productivity retain valid information after such a high degree of loss in the upper reactive zone of the sediment. However, a number of studies have found that historic or isotopically reconstructed records of aquatic productivity are reflected in organic biomarker signals (e.g., Prahl, 1992; Prahl et al., 1989; Kennedy and Brassel, 1991; Jasper and Gagosian, 1993). In summary, although compositional changes in the surface sediments (0–10 cm) are probably diagenetic in origin, below this chemically dynamic zone, the changes appear to be depositional in origin. The organic biomarker profiles thus reflect progressively increasing production of planktonic and microbially derived OM over the past 60 years.

Questions still remain, however, concerning geochemical changes that occur immediately across the 1934 sediment horizon. While BSi and TOC abruptly increase reflecting an increase in water column productivity, TOC-normalized phytoplankton biomarker abundances do not show abrupt increases across this horizon. Apparently, the increase in phytoplankton and microbially derived OM was proportional to the increase in TOC at this time. Another possible inconsistency is that while lipid diagenetic indicators (Fig. 9) are not significantly different across the 1934 horizon, the C/N ratio does increase abruptly upcore. The observed increase in the C/N ratio of OM, however, may be due to a change in the type, or nutritional status of phytoplankton-derived OM. The concentration of sedimentary TN, too, may be altered by other redox-sensitive processes such as ammonification and denitrification. At present, the significance of the abrupt increase in C/N at the 1934 horizon is unclear.

4.2.3. Summary of indicators

To assess the changes in OM sources to the sediments that have occurred over the time represented by this core, an index of source contribution (a weighted mean of biomarker concentrations for

each OM source) was assembled from all the biomarker compound distributions listed above. Enrichment factors were then calculated by normalizing each of these indices to the mean found in the lower (below 100 cm) portion of the core, such that a value of unity represents no increase in an OM source since 1934 (Fig. 10a). The first appearance of OM enrichment in plankton and microbially derived material begins after 1934 coincident with inorganic indicators of increased productivity (BSi and TOC) and hypoxia (AVS/NAVS). Between 1948 and 1975, plankton and microbial OM sources have increased relative to earlier periods by factors of between 2 and 4. Since 1975, we find 4- to 12-fold enrichments in these OM sources. The timing and magnitude of the change in productivity are consistent with long-term trends in surface chlorophyll, which have increased by roughly 2-fold during the last 50 years in the mid-Bay region (Harding and Perry, 1997). It has been estimated that a 15-fold increase in inorganic nitrogen since pre-industrial times has led to a doubling of phytoplankton production in Narragansett Bay, Rhode Island (Nixon, 1997). For CB, it is estimated that nitrogen loading has increased by 5–8 times and phosphorous loading by 13–24 times since pre-colonial times (Boyton et al., 1995). So, a doubling of autotrophic production in CB might also be predicted.

The organic and inorganic geochemical changes that we observe appear contemporaneously with an increase in the use of inorganic fertilizers in the state of Maryland and the United States in general (Fig. 10b) when synthetic nitrogen fertilizers were first introduced in the 1940s (Vitousek et al., 1997). Increases in fixed nitrogen loadings derived from all sources including atmospheric deposition occurred in the 1930s and 1940s to most northeastern coastal waters (Jaworski et al., 1997). Although the increased nutrient loadings, anoxia/hypoxia indicators, and OM deposition and preservation appear synchronously, a single 'cause and effect' relationship should not be made because other probable changes such as increases in sewage input, urbanization, oyster harvesting and animal husbandry, all linked with increasing human population growth rate (Fig. 10b), occurred at the same time in the CB watershed and in most parts of the eastern United States (Dodd, 1993). Further, this work was based

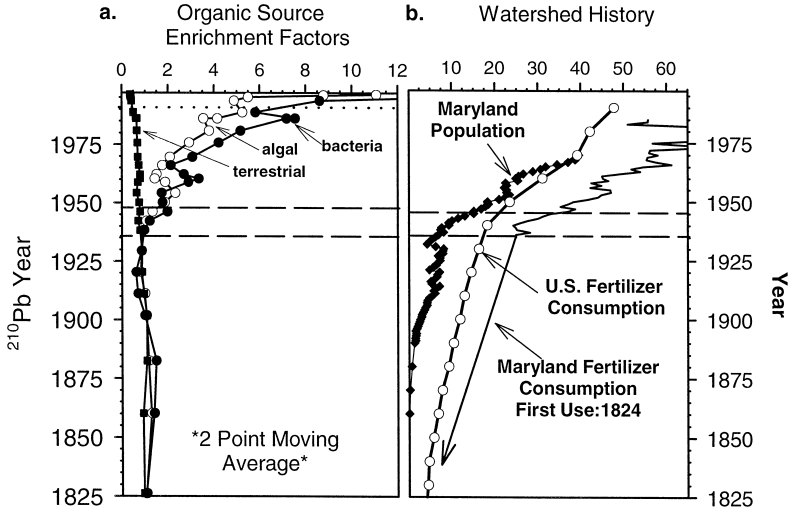

Fig. 10. (a) Downcore enrichment factors of OM derived from phytoplankton (open circles), bacterial (filled circles) and terrestrial (filled squares) sources. Enrichment factors are means of all biomarker compounds concentrations (equally weighted) mentioned in text for each OM source and normalized to lower core (below 100 cm depth) average. These plots were smoothed by a two-point moving average. (b) Historic record of commercial fertilizer consumption in the United States ($\times 10^6$ t yr^{-1}) (U.S. Bureau of the Census, 1975) and the State of Maryland ($\times 6000$ t yr^{-1}) (Cornwell et al., 1996) and human population in Maryland ($\times 10^5$) (Dodd, 1993).

upon the geochemical record of a single core in the mesohaline region of the Bay; additional work will be undertaken to extend these findings to other portions of the estuary.

5. Conclusions

Many paleoenvironmental reconstruction studies rely on one or a few inorganic or bulk organic chemical indicators of environmental change. However, in the estuarine environment, physical and geochemical conditions of deposition may change on short time scales and there exists a variety of possible sources of OM whose quality may also change on short time scales. It is for this reason that a combined inorganic and lipid geochemical analysis approach, along with diagenetic modeling, has proved itself to be useful, even necessary, when working in the estuarine environment.

Our data indicate that major changes in bottom water oxygenation conditions and organic carbon deposition in the mesohaline portion of CB began rather abruptly between 1934 and 1948. TOC delivery and storage increased abruptly at this time and remain in excess of that predicted by diagenetic models. Although it remains uncertain whether increased water-column productivity or decreased water column mineralization or both, are the cause of this shift, the combination of inorganic and organic productivity indicators (biogenic silica and phytoplankton-derived lipids increase concurrently) point toward the former explanation. Not only has OM storage increased, but a qualitative change, toward organic carbon derived increasingly from plankton and microbial sources, has occurred. These changes in OM composition are also not predicted by diagenetic modeling. Increased phytoplankton and zooplankton production is the likely cause of these changes. Fluctuations in the sources of organic carbon deposited in mesohaline CB sediments indicate an increased availability of labile forms of OM to higher organisms with potential consequences for the trophic balance of the estuary. These findings demonstrate that anthropogenic activities within estuarine watersheds can exert a substantial influence on carbon cycling processes in estuaries. Impacts on carbon cycling and the ecology of the coastal ocean are also possible to the extent that estuarine productivity may be subsequently exported.

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