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Bulk Organic Matter and Lipid Biomarker Composition of Chesapeake Bay Surficial Sediments as Indicators of Environmental Processes

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Seasonal measurements of lipid biomarker (fatty acid and sterol) composition along with organic carbon and nitrogen elemental and stable isotopic signatures were made in surficial sediments collected along the salinity gradient of the Chesapeake Bay mainstem. These data along with water quality information including chlorophyll and dissolved oxygen concentration were used to assess temporal and spatial variations in organic matter (OM) composition and the processes that control its distribution. While the amount of OM in sediments was largely related to sediment surface area and exhibited very little seasonal variability, OM lipid composition was spatially and temporally variable. Principal components analysis (PCA) identified three suites of lipid compounds that encapsulate these elements of variability. The first, representing allochthonous versus autochthonous OM identified the Northern Bay as the major site of terrestrial OM deposition. The greater contribution of terrestrial OM in this region was supported by elemental C:N and stable isotope data. The second was identified as a seasonal component of lipid composition and indicated the deposition of labile, primarily diatom-derived OM in the spring and degradation of this OM through the summer and fall. This component was particularly enriched in Southern Bay sediments relative to other portions of the Bay and varied with tributary water inflow. A third component of OM composition represented microbially-derived OM which, although most abundant in the Mid-Bay, represented the greatest fraction of OM in the Southern Bay. Sediments of the Mid-Bay were particularly enriched in flagellate-derived OM in the summer. Sediment OM composition was not influenced by water-column dissolved oxygen concentration. The combination of lipid biomarkers and PCA proved a more sensitive indicator of sediment OM sources and reactivity than bulk elemental or isotopic data and presents a picture of the estuary as a trap for both allochthonous and autochthonous OM. The high degree of spatial and temporal variability in estuarine sediment OM composition may influence the distribution of benthic communities and the long-term sediment record.

Keywords: estuaries; estuarine sedimentation; organic matter; lipids; Chesapeake Bay

Introduction

Although estuaries represent only a small portion of the total coastal ocean their high primary productivity and position as receivers of terrestrial organic matter (OM) gives these regions an important role in the global cycling of organic carbon. As estuaries will be susceptible to alteration in the coming years due to sea-level rise or anthropogenic influence (Smith & Hollibaugh, 1993), it is important that we understand the functioning of these systems at present. The fate of autochthonous and terrestrially derived OM in estuarine environments, however, is not well understood (Hedges *et al.*, 1997; Smith & Hollibaugh, 1993). Particulate OM may be trapped within the estuary (i.e. deposited and stored in sediments), biologically utilized within the water column and surface sediments by heterotrophic organisms, or exported to the ocean. Furthermore, the character of OM may be altered by heterotrophic activity or chemical processes such as desorption or photolysis prior to deposition or export. Not only is the knowledge of OM storage in estuaries an important part of our understanding of the marine carbon budget, but the distribution of OM from various sources will influence the availability of food sources for pelagic and benthic food webs (Boon *et al.*, 1999; Diaz & Schaffner, 1990) and may affect the distribution of contaminants (Karickoff *et al.*, 1979).

An impediment to our understanding of these processes has been the extreme temporal and spatial heterogeneity that characterizes estuaries (see Hedges & Keil, 1999). Physical, chemical and biological regimes within estuaries can vary spatially on scales of

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a few kilometres and temporally on scales ranging from hours (due to tidal forcing) to years or greater. Biological productivity, water column respiration, seasonal anoxia, freshwater inflow and sediment type, all of which may vary seasonally, annually and at a variety of spatial scales, may influence the type and amount of OM that is deposited, remineralized or exported.

Understanding the cycling of organic carbon within estuaries takes on further importance because, among marine environments, these systems are most likely to have been altered by human activities in recent centuries (Holligan & Reiners, 1992). Both eutrophication and water column anoxia have become major environmental concerns in recent years (Diaz & Rosenberg, 1995; Nixon, 1995). Cultural eutrophication has altered the cycling of organic carbon and the phytoplankton community distribution in many estuaries and coastal regions during this century (Cooper & Brush, 1991; Eadie *et al.*, 1994; Zimmerman & Canuel, 2000). Labile carbon produced by algal blooms, if remineralized within the estuary, either in the water column or sediments, is likely to be an important sink for dissolved oxygen. Depending upon the timing and extent of remineralization, labile OM can also be an additional source of nutrients to the water column, thus fueling further productivity. While some algal blooms such as diatoms occur predominantly in the spring, other taxa are dominant during the warm summer months (e.g. dinoflagellates, cryptomonads, chlorophyceans and cyanobacteria; Marshall & Alden, 1993). Other potential contributors of OM to the estuary include bacteria and terrestrially-derived OM. While the highest heterotrophic bacterioplankton production and abundances occur in the summer with increasing temperature (Shiah & Ducklow, 1994) the influx of terrestrial OM may be linked to tributary flow rates that tend to be highest in the spring. As integrators of water column processes occurring over periods of a few days to months, surficial sediments may contain a key record that can improve our understanding of estuarine carbon cycling and the influence of eutrophication and water column anoxia. Further, in order to interpret the paleo-record of environmental change contained in sediment cores, we must first understand to what extent water column processes are recorded in surficial sediments and how OM is cycled within this zone prior to long-term preservation.

Lipid biomarkers have the potential to identify the major sources and timing of OM delivery to, and remineralization within sediments. Due to their structural diversity, source specificity and relative stability, lipid biomarkers have proved to be useful tools for assessing the sources and fates of OM to marine (Prahl *et al.*, 1994; Wakeham & Canuel, 1988), coastal (Boon *et al.*, 1999; Dachs *et al.*, 1999; Yunker *et al.*, 1995), and estuarine systems (Canuel *et al.*, 1995; Laureillard & Saliot, 1993; Mudge & Norris, 1997). Previous studies examining estuarine OM composition using biomarkers have been carried out at various spatial and temporal scales. The goal of this research is to examine spatio-temporal variability in the quantity and quality of OM deposited to estuarine sediments over seasonal time-scales and estuary-length spatial scales. Because of the size and complexity of data sets of this type, some form of multivariate data analysis is necessary to deconvolute the dominant sources of variability. Principal components analysis (PCA) is such a tool and has been used successfully to interpret organic and inorganic chemometric data (Meglen, 1992; Mudge & Norris, 1997; Yunker *et al.*, 1995). An advantage of this form of data analysis is that the variance associated with a single variable can be apportioned between a number of factors. The source specificity of certain biomarker compounds or compound groups can, therefore, be evaluated and non-specific distributions can be incorporated into the interpretation of OM compositional distribution.

This study was carried out in Chesapeake Bay (CB), the largest estuary in the United States (11 500 km^2) with a drainage basin that encompasses an area (165 760 km^2) from southern New York State to western Virginia. A number of major tributaries flow into CB but the Susquehanna River, at the head of the Bay, contributes the majority of the freshwater (60%), dissolved inorganic nitrogen (80%; Harding & Perry, 1997) and sediment (61%; Officer *et al.*, 1984) entering the Bay. CB is classified as a partially mixed estuary in which tides are the primary energy source driving water circulation. Surface sediments were collected and water quality parameters were measured along a transect from the head to the mouth of CB seasonally over two years. In the present study, carbon and nitrogen stable isotopic and elemental signatures and lipid biomarker compounds (fatty acid and sterols) are used to identify variations in the sources, quality and amount of OM deposited to CB surface sediments and to identify the dominant estuarine processes that control their distribution.

Materials and methods

Sample collection

The majority of the surface sediment samples were collected during five cruises on 6–9 November of 1995 and 11–15 March, 29 April–1 May, 9–11 July and 24–26 September of 1996. Samples were

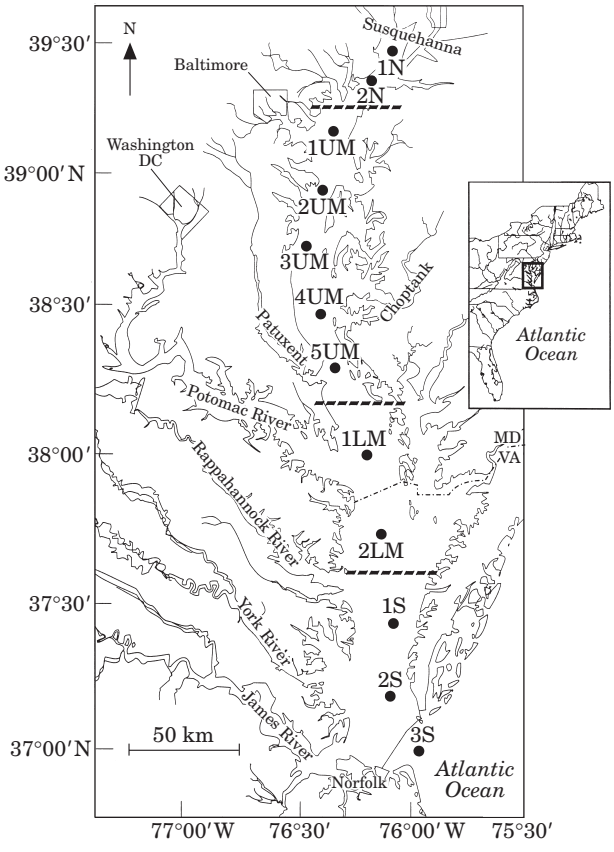

FIGURE 1. Map of Chesapeake Bay showing sampling station locations. Dashed horizontal lines separate the North Bay (N), Upper Mid-Bay (UM), Lower Mid-Bay (LM) and South Bay (S) regions as defined in this study. The turbidity maximum is generally located between 2N and 1UM.

collected from 12 sites along the Bay's central axis, a 12–30 m channel running the length of the CB mainstem (Figure 1; Table 1). Additional samples were collected during 1995 and 1997 from two stations, 2LM and 1S, in order to assess interannual variability in OM composition at these sites. Sites were chosen which have been previously used by us and other researchers so that comparisons could be made and correspond to the site names; 1N:SUS, 2N:922Y, 1UM:904N, 2UM:858, 3UM:834G, 4UM:M3, 5UM:818P, 1LM:804C, 2LM:CB5.4, 1S:CB6.3, 2S:CB7.3, and 3S:CB8.1.

Surface sediments were collected using a box corer (Ocean Instruments, San Diego, CA, U.S.A.). Water overlying the sediments was removed by siphon and the upper 0·25 cm of sediment was transferred to pre-combusted (450 °C for 5 h) glass jars using a solvent-rinsed spatula. Benthic organisms and sediment surrounding worm tubes were excluded from collection. Sediment samples were stored on ice while aboard ship and transferred to an ultracold freezer (− 80 °C) for storage upon return to the laboratory. Water column information was collected at each site using a conductivity-temperature-depth (CTD) continuous profiling instrument with an oxygen electrode and *in vivo* fluorometer (Curling & Neilson, 1994). Water for chlorophyll *a* (chl *a*) measurements was pumped from 1 m below the water surface and 1 m above the sediment surface from tubing attached to the CTD and collected onto 47 mm glass-fiber filters that were immediately frozen. Additional chl *a* and primary productivity rate data were obtained from the website of the Chesapeake Bay Program (CBP, 2000) and from The University of Maryland TIES monitoring program (J. Hagy, pers. comm.). The data obtained from these sources were collected at times within two to four days of our sample collections, and at locations within a few kilometers of the sample sites used in this study.

Chemical analyses

Detailed descriptions of the analytical methods used for this study may be found in Zimmerman (2000) but shall be described briefly here. Filters for chl *a* measurement were extracted in acetone and analysed by UV/VIS scanning spectrophotometer (Milton Roy Spectronic 1201) with methods described in Parsons *et al.* (1984). Sediments were analysed for total organic carbon (TOC) and nitrogen (TN) content following the methods of Hedges and Stern (1979). Dried sediments were ground, acidified with HCl and analysed using a Carlo Erba NA1500 elemental analyser. Stable isotope analyses were carried out on dried and acidified sediment samples at the University of California, Davis-Stable Isotope Facility by isotope ratio mass spectrometric analysis using a continuous flow system with on-line sample combustion (Europa Scientific Integra). Carbon and nitrogen isotopic values are expressed in standard delta notation relative to PeeDee Belemnite and atmospheric nitrogen standards, respectively. Both elemental and stable isotope samples were analysed in duplicate and a third sample was analysed if duplicates did not agree within 10%. Sediment surface area was determined by BET analysis (Micromeritics, Gemini III 2375 Analyser). This method measures N_2 adsorption below saturation pressure using multi-point adsorption isotherms with pure kaolinite serving as a standard. Sediment surface area data for the November 1995 sediments were provided by Dr L. Mayer (University of Maine) and were comparable to our measurements.

The lipid composition of sediments from nine stations was analysed within one year of each cruise following the methods of Canuel and Martens (1993).

TABLE 1. Study site water column characteristics and bulk sediment properties

Sample #	Collection date	Site	Latitude (°N)	Longitude (°W)	Depth (m)	Sed. surf. area ($m^2\ g^{-1}$)	Bottom salinity	Bottom O_2 ($mg\ l^{-1}$)	Surface chl *a* ($\mu g\ l^{-1}$)	Deep chl *a* ($\mu g\ l^{-1}$)	CBP* chl *a* ($\mu g\ l^{-1}$)	CBP* productivity ($\mu g\ C\ l^{-1}\ h^{-1}$)	$\%C_{org}$	%N	$C:N_a$	$\delta^{15}N$ (‰)	$\delta^{13}C$ (‰)
1	07-Nov-95	1N	39·55	76·08	14	3·10	0·1	12·00			4·66	17·58	1·33	0·09	16·43	5·59	−26·03
2	30-Apr-96	1N					0·2	10·50	18·29	21·41	6·00	14·78	1·55	0·13	14·33	5·30	−39·74
3	10-Jul-96	1N				5·25	0·1	6·20	18·29	21·41	7·98	52·78	3·00	0·15	23·74	5·94	−25·28
4	25-Sep-96	1N					0·1	8·90	12·28	9·37	15·66	65·34	1·58	0·12	16·02	5·59	−25·28
5	07-Nov-95	2N	39·37	76·13	10	27·33	0·2	12·40			5·48	19·26	3·84	0·21	20·96	6·51	−24·99
6	13-Mar-96	2N					2·1	9·40	2·61		3·65	11·30	5·04	0·27	22·18	5·76	−25·11
7	30-Apr-96	2N					0·1	9·40	11·01	124·53	6·45	18·95	3·84	0·21	20·96		
8	10-Jul-96	2N					0·1	6·30	10·17	7·93	9·50	64·60	3·06	0·18	20·33	6·76	−24·66
9	25-Sep-96	2N					0·1	8·55	8·54	12·83	23·60	189·40	3·31	0·19	20·25	5·42	−25·01
10	07-Nov-95	2UM	38·96	76·38	15	20·37	15·5	8·00			9·44	62·34	3·76	0·50	8·84	9·25	−22·3
11	13-Mar-96	2UM					17·1	7·00	112·15		34·38	55·65	3·67	0·45	9·43	8·46	−22·56
12	30-Apr-96	2UM					10·9	1·10	4·12	3·57	9·10	33·08	2·98	0·30	11·64	7·38	−23·38
13	10-Jul-96	2UM					17·2	0·00	0·00	3·27	7·90	64·40	3·45	0·45	9·04	7·74	−23·32
14	25-Sep-96	2UM					16·6	0·20	15·50	2·04	13·70	82·22	3·24	0·35	10·80	8·02	−23·96
15	07-Nov-95	4UM	38·57	76·45	15	15·37	18·9	7·60			6·78	29·12	3·90	0·54	8·36	8·98	−22·45
16	13-Mar-96	4UM					15·0	12·00	3·21		7·65	5·25	3·89	0·52	8·68	9·65	−21·77
17	30-Apr-96	4UM					11·8	3·95	14·48	13·06	9·82	54·30	4·14	0·57	8·55	8·41	−22·63
18	10-Jul-96	4UM					18·3	0·00	10·07	2·49	11·48	27·20	3·75	0·50	8·69	8·69	−22·05
19	25-Sep-96	4UM					14·7	4·25	4·90	11·17	6·03	45·40	3·64	0·48	8·83	8·60	−21·94
20	07-Nov-95	1LM	38·06	76·06	22	25·22	20·9	7·90			8·30	53·70	3·21	0·41	9·12	7·86	−21·62
21	13-Mar-96	1LM					14·5	13·00	2·80		11·70	12·65	2·42	0·31	9·00	8·21	−21·56
22	30-Apr-96	1LM					15·4	5·40	21·40	8·20	18·30	110·95	3·06	0·41	8·69	8·01	−21·52
23	10-Jul-96	1LM					17·8	0·00	14·92	2·15	22·00	125·47	3·07	0·40	8·89	7·74	−20·71
24	25-Sep-96	1LM					15·8	2·90	7·80	1·44	12·13	61·43	3·43	0·48	8·36	8·54	−21·84
25	08-May-95	2LM	37·80	76·18	33		24·5	5·6	4·93	2·00	2·21	1·91	2·33	0·37	7·38		
26	18-Jul-95	2LM					22·3	1·3	0·72	0·00		1·06	2·39	0·35	7·98		
27	18-Sep-95	2LM					23·8	4·91	4·55	5·34	3·50	9·38	2·50	0·37	7·82		
28	14-Mar-96	2LM				10·23	16·7	12·90	4·06	19·22	6·90	2·92	2·40	0·37	7·57	8·45	−21·39
29	29-Apr-96	2LM				9·67	16·4	7·00	33·20	22·32	18·91	10·64	2·78	0·36	8·99	7·90	−22·61
30	18-Jun-96	2LM				10·86	18·5	0·00	8·40	1·26	9·95	11·45	3·20	0·43	8·60	6·14	−20·96
31	10-Jul-96	2LM				12·16	19·9	0·70	14·01	0·80	14·88	13·20	2·89	0·38	8·89	6·84	−20·58
32	25-Sep-96	2LM				11·65	15·4	6·40	14·27	4·07	14·52	19·31	2·90	0·39	8·73	7·03	−21·25
33	14-Oct-96	2LM				12·09	18·3	8·00	12·26	3·97	20·02	21·12	3·03	0·41	8·64	7·79	−21·03
34	04-Apr-97	2LM				12·05	15·5	10·00	20·51	56·82	32·27	88·77	2·52	0·33	9·05	8·01	−21·04
35	10-Aug-97	2LM					22·6	4·00			4·66	27·47	2·62	0·34	8·93	7·49	−20·93

TABLE 1. *Continued*

Sample #	Collection date	Site	Latitude (°N)	Longitude (°W)	Depth (m)	Sed. surf. area ($m^2\ g^{-1}$)	Bottom salinity	Bottom O_2 ($mg\ l^{-1}$)	Surface chl *a* ($\mu g\ l^{-1}$)	Deep chl *a* ($\mu g\ l^{-1}$)	CBP* chl *a* ($\mu g\ l^{-1}$)	CBP* productivity ($\mu g\ C\ l^{-1}\ h^{-1}$)	$\%C_{org}$	%N	$C:N_a$	$\delta^{15}N$ (‰)	$\delta^{13}C$ (‰)
36	08-May-95	1S	37·41	76·16	12	1·03	23·2	7·4	1·45	2·93	3·31	1·45	0·57	0·09	7·69		
37	18-Jul-95	1S					25·4	2·12	2·77	0·00	8·93	2·73	0·59	0·16	4·32		
38	18-Sep-95	1S					22·3	6·63	2·82	2·21	1·66	3·44	0·43	0·06	8·15		
39	14-Mar-96	1S					23·6	12·60	5·98	39·94	6·40	5·32	1·02	0·11	11·00	8·06	−20·72
40	07-Nov-95	2S	37·12	76·13	13	1·23	27·4	8·50			39·32	11·25	0·19	0·02	8·98	6·91	−21·62
41	13-Mar-96	2S					31·1	11·60	5·00		5·94	5·10	0·29	0·04	8·52	8·33	−20·44
42	30-Apr-96	2S					29·4	11·60	40·95	12·92	45·00	17·60	0·40	0·05	8·66	7·45	−20·41
43	10-Jul-96	2S					27·9	7·20	5·26	1·47	14·26	6·92	0·27	0·04	8·73	7·58	−20·37
44	25-Sep-96	2S					25·1	6·50	3·75	1·45	4·75	11·08	0·32	0·04	8·73	7·12	−20·75
45	07-Nov-95	3S	36·95	76·03	19	1·11	30·9	7·80			6·10	2·63	0·23	0·03	10·00	6·99	−20·58
46	13-Mar-96	3S					31·8	13·00	8·33		7·05	5·19	0·37	0·04	9·84	7·47	−19·95
47	30-Apr-96	3S					31·4	11·85	21·57	3·91	8·25	8·77	0·17	0·02	9·83	7·19	−20·47
48	10-Jul-96	3S					26·4	6·60	6·20	2·08	6·49	6·77	0·23	0·03	10·55	6·79	−20·95
49	25-Sep-96	3S					28·9	6·25	7·75	5·62	3·73	8·52	0·43	0·05	9·71	6·92	−21·03
Additional stations without lipid analyses																	
50	07-Nov-95	1S	37·41	76·16	12	1·03	23·7	8·80			2·37	2·99	0·31	0·03	12·30	8·05	−20·74
51	07-Nov-95	2LM	37·80	76·18	33	15·92	22·6	8·60			7·85	8·63	2·36	0·29	9·49	8·25	−21·50
52	07-Nov-95	5UM	38·31	76·29	33	17·54	20·7	7·70			6·78	29·12	1·49	0·18	9·60	8·97	−21·86
53	07-Nov-95	3UM	38·72	76·44	17	15·94	18·9	7·60			6·78	29·12	3·57	0·49	8·47	10·55	−22·04
54	07-Nov-95	1UM	39·07	76·33	11	19·81	3·6	8·80			9·44	62·34	3·77	0·45	9·74	9·74	−22·54

*Chesapeake Bay Program website (CBP, 2000) for mean surface waters (above the pycnocline) composite sample.

Briefly, sediments were thawed, homogenized and transferred (10 g wet wt) to a chloroform:methanol (2:1, v:v) solution for extraction aided by sonication. Extracts were then saponified in KOH and re-extracted into hexane under basic and acidic conditions. After methylation of the acid portion using BF_3-methanol and a purification procedure using silica gel chromatography, fatty acid methyl esters (FAME) and sterols (as TMS ethers) were analysed by gas chromatography (GC) using direct injection onto a 30 m × 0·32 mm i.d. DB-5 fused silica capillary column (J & W Scientific) with a flame ionization detector. Individual peaks were identified based on relative retention times of known standards and peak areas were quantified relative to internal standards added just prior to GC analysis (methyl heneicosanoate for fatty acids and 5α(H)-cholestane for sterols). Compound identifications were confirmed by gas chromatography-mass spectrometry (Hewlett Packard 6890 Series).

Data analysis

Data were statistically analysed using MiniTab (MiniTab Inc.; release 12.1, 1998) software. In cases where our data were not normally distributed or not of homogeneous variance, non-parametric analysis was employed in addition to parametric analysis. Within MiniTab, the ' General Linear Model ' analysis of variance (ANOVA) was used. A Tukey pairwise comparison test and the non-parametric test for difference of medians (Kruskall–Wallis Test) were used to test the effects of region, season, water column productivity, and dissolved oxygen (DO) concentration. Regions were blocked as follows based on salinity zonation, tidal regime and sediment-type similarity: 1N and 2N (North Bay), sites between 1UM and 5UM (Upper Mid-Bay), 1LM and 2LM (Lower Mid-Bay), and sites between 1S and 3S (South Bay). Seasons were blocked as follows: March–May (spring), June–August (summer), and September–November (fall). Water column productivity was blocked as follows: 0–15 (low), 15–50 (medium) and >50 mg C l^{-1} hr^{-1} (high). DO concentration was blocked as follows: 0–2 (anoxic), 2–5 (hypoxic) and >5 mg l^{-1} O_2 (oxic). Interdependence of variables was tested using MiniTab software that calculates the Pearson product moment correlation coefficient to measure the degree of linear relationship and performs a two-tailed test of the correlation.

PCA was also employed to reduce the complexity of the data set (i.e. identify a small number of variables that account for a large proportion of the total variance in the original variables). The PCA method projects the multidimensional space of the data onto a space of fewer dimensions (Zitco, 1994). The orthogonal axes of this new space are the ' principal components ' that can, themselves, be described by a linear combination of the original variables. The principal components of the data can help to explain the underlying data structure (i.e. relationships among samples or variables). Further descriptions of the mathematics and interpretation of PCA can be found in Meglen (1992). Only those variables with mean values and standard deviations of similar magnitude (Johansson & Sjodin, 1984) were selected for PCA. MiniTab software automatically standardizes the variables by subtracting the mean and dividing by their standard deviation and then calculates the principal components using the normalized correlation matrix.

Results

Water column parameters

A wide range of environmental conditions occurred during the period of this study. For example, while 1995 and 1997 were relatively dry years with low freshwater discharge (average daily flow of the Susquehanna at Conowingo, Md. of 794 and 841 m^3 s^{-1}, respectively), 1996 water inflow was at a record high (average daily flow of 1797 m^3 s^{-1}). As a result, nutrient loading to the Bay was much higher during 1996 and led to a dramatic spring bloom event (Harding & Perry, 1997).

Chl *a* concentrations usually ranged from <1 to 20 µg l^{-1} in surface (1 m below surface) and deep (1 m above bottom) waters during the study period (Table 1). However, a number of chl *a* concentrations >20 µg l^{-1} were recorded, all of which occurred during spring samplings (March and April). Maximum chl *a* concentrations were generally found in the surface waters of the Mid-Bay as previous studies have observed (Fisher *et al.*, 1998; Fisher *et al.*, 1988) and can be attributed to phytoplankton utilization of riverine nutrients downstream of the turbidity maximum. Our surface chl *a* concentration measurements were positively correlated with those of the CBP (2000) so data from this source were used in statistical analyses when chl *a* was not determined on our cruises.

Rates of surface water primary productivity (CBP, 2000) ranged from 1 to 190 µg C l^{-1} h^{-1} (mean ± SD = 32 ± 37 µg C $l^{-1}h^{-1}$) but were generally highest in the Mid- and North Bay and during the summer and fall as is characteristic of CB (Malone *et al.*, 1988). Hypoxic or anoxic bottom water conditions were recorded during every summer sampling at sites

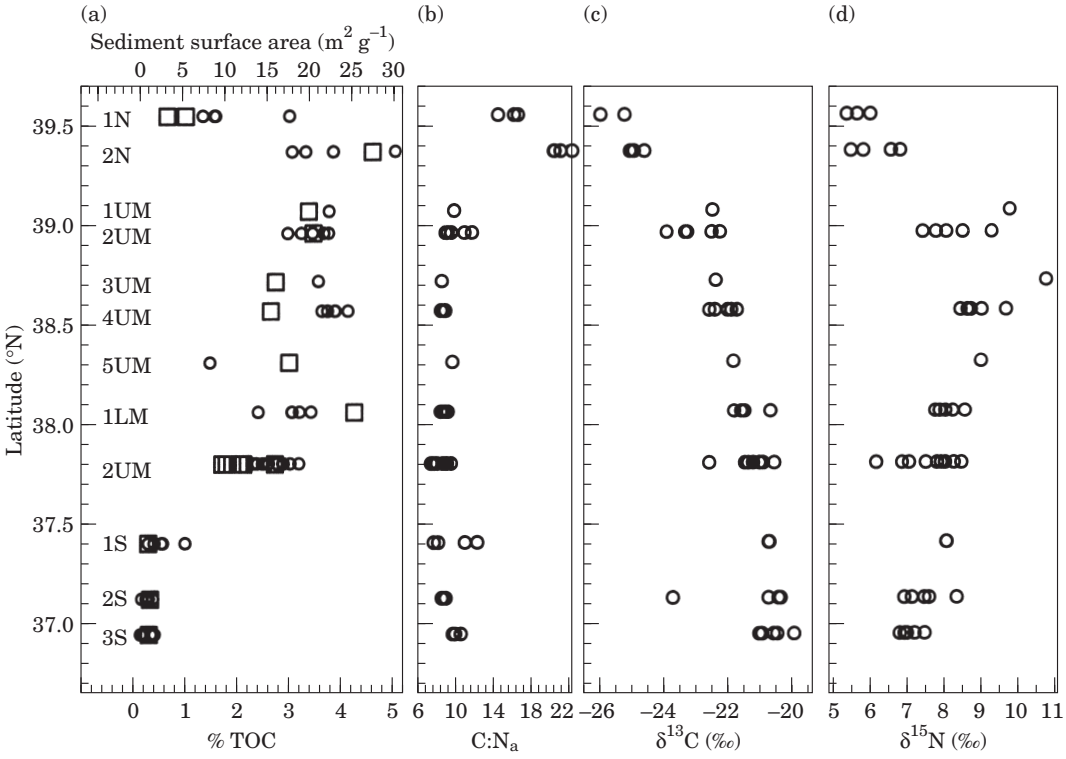

FIGURE 2. Spatial distribution of (a) total organic carbon content (%, open circles) and sediment surface area (m2 g-1, open squares), (b) organic carbon:total nitrogen (molar) ratio, (c) carbon stable isotope and (d) nitrogen stable isotope composition of Chesapeake Bay surface sediments.

2UM through 1S and occasionally in September (Table 1). Given the wide range of hydrodynamic and biological conditions that were observed, it is likely that our study encompassed a time period in which ample variability in OM supply and composition can be occurred.

Bulk sediment composition

Surface sediment TOC concentrations [Figure 2(a)] displayed a range of values (0·3–5·0%) with the lowest values found in the sandier South Bay and the northernmost station (1N) and exhibited greater spatial than temporal variability. No significant difference (ANOVA) was found between the mean TOC blocked by season or DO level in the Whole-Bay or Mid-Bay-only data sets. However, regional differences in TOC concentration were significant (P <0·001) with the highest found in the Upper Mid-Bay and the lowest in the South Bay. Although TOC was significantly correlated with surface water productivity (r=0·43, P<0·001), the strongest relationship was found between TOC and sediment surface area (r=0·80, P<0·001). The correlation between TOC and productivity may be spurious since there was no significant relationship between these variables in site 2LM or Mid-Bay-only data. Like TOC content, sediment surface area displayed little seasonal (examined at site 2LM only) but significant (P=0·004) regional variability [Table 1, Figure 2(a)].

Surface sediment TN concentrations displayed distributions very similar to that of sediment TOC except at site 2N where TN content was disproportionately low. The elemental ratio of TOC to TN expressed on a molar basis ($C:N_a$) was consistently between 8 and 10 in most of the Bay [Figure 2(b)], indicative of a mainly algal OM source (Meyers, 1994). Elevated $C:N_a$ ratios of between 14 and 22 at the two northern sites and 11 to 12 at 1S may indicate some contribution of OM derived from terrestrial sources or older reworked material. TN was correlated with TOC (r=0·86, P<0·001) and the distribution of TN was influenced by the same factors as TOC (i.e. sediment surface area, but not water column productivity) and was not seasonally variable.

A distinct stable isotope signature ($\delta^{13}C$ and $\delta^{15}N$) was found for surface sediments in each region of the bay. North Bay surface sediments had the most depleted carbon (-25 to -26‰; [Figure 2(c)] and nitrogen [5·3–6·8‰; Figure 2(d)] isotopic

signatures consistent with some contribution from terrestrial or vascular plant sources. The $\delta^{13}C$ signature of the surface sediment increases progressively southward through the estuary while the $\delta^{15}N$ signature is most enriched in the Upper Mid-Bay and decreases southward. No seasonal trends or oxygen concentration dependence (ANOVA) were noted in the isotope data. Although $\delta^{13}C$ values were significantly depleted at sites with high overlying water column productivity ($P=0{\cdot}002$) in the Bay as a whole, this relationship was not evident in Mid-Bay-only data. Both $\delta^{13}C$ and $\delta^{15}N$ were negatively correlated with the $C:N_a$ ratio ($r=-0{\cdot}51$ and $-0{\cdot}64$, respectively; $P<0{\cdot}001$) and $\delta^{15}N$ was positively correlated with sediment TN concentration ($r=0{\cdot}55$, $P<0{\cdot}001$).

Sediment lipid composition

Sixty-five individual fatty acids (FA) and 24 sterol compounds were identified in CB surface sediments representing a range of OM sources (Table 2). Only the compound or compound groups listed in Tables 3 and 4 were used for interpretation and were selected because of their greater relative abundance, confidence in identification and because unambiguous source assignments could be made (i.e. they are biomarkers for likely contributors of OM to CB sediments). A complete data table may be found in Zimmerman (2000). The FA listed in Table 3 represent an average of $58 \pm 7\%$ of the total FA composition in each sample. Total FA concentrations ranged from 12 to 873 $\mu g\ g^{-1}$ dry sediment with the highest concentrations in the Upper and Lower Mid-Bay (mean $\pm$ SD $= 471 \pm 211\ \mu g\ g^{-1}$ and $290 \pm 160\ \mu g\ g^{-1}$, respectively) and the lowest in the North and South Bay ($82 \pm 35\ \mu g\ g^{-1}$ and $47 \pm 43\ \mu g\ g^{-1}$, respectively). The high standard deviations among these concentrations are not surprising given the substantial variability in environmental parameters and sediment type represented within the data set.

Total sterol concentrations ranged from 4 to 276 $\mu g\ g^{-1}$ sediment (Table 4). Again, the highest concentrations were in the Upper Mid-Bay and Lower Mid-Bay (mean $\pm$ SD $= 198 \pm 52\ \mu g\ g^{-1}$ and $106 \pm 71\ \mu g\ g^{-1}$, respectively) and the lowest concentrations found in the North and South Bay ($33 \pm 23\ \mu g\ g^{-1}$ and $10 \pm 5\ \mu g\ g^{-1}$, respectively). The sterols listed in Table 4 represent 50–84% (mean $= 68 \pm 8\%$) of the total sterols present in the sediments. The sterol compounds were comprised of C_{27}, C_{28}, and C_{29} moieties in the average proportions of 25%, 32% and 26%, respectively. The greatest relative proportion of C_{29} sterols (generally of vascular plant origin) were found consistently in North Bay samples while the greatest proportion of C_{28} sterols (plankton sources) were found generally in Mid-Bay samples.

Expressed in units of $\mu g\ g^{-1}$ dry sediment, nearly every FA and sterol compound and group concentration was positively correlated with every other FA and sterol (except the even-numbered long-chain saturated FA and the C_{24} alcohol). In addition, each of these was directly correlated with sediment TOC, surface area and, in many cases, surface water chl *a* concentration. Thus, these relationships are likely driven by the total OM input variations to each region of the Bay. Another way to elucidate spatial and temporal patterns of OM source variability is to examine biomarker compositions expressed on a relative percent basis. Each FA or sterol compound or group is expressed as a relative weight percent. One advantage of this approach is that, due to variation in extraction efficiency, a compound's relative abundance can be known more accurately than its absolute concentration. Also, small changes in OM source contribution may be more easily detected since lipids often make up only a small fraction of the TOC. The effects of closure (interdependence of variables), a disadvantage associated with this approach, were minimized by normalizing individual FA and sterol compound concentrations to total FA and sterols, respectively and by using compounds that do not represent major portions of their compound class.

Intercorrelation of only those biomarkers derived from similar sources, when expressed as relative percent concentrations, support their source assignments. For example, the proposed terrestrial biomarkers (LCFA, 24OH, 29Δ5,22 and 29Δ5; key to abbreviations in Table 2) are all significantly and positively intercorrelated (and are not generally correlated with the algal biomarkers). The relative abundance of the bacterial markers 15,17 Br and 10 MeBr are significantly correlated with one another but are not correlated with ΣHOP. ΣHOP is correlated, instead, with the dinoflagellate markers 30Δ22 and 30Δ0 ($P=0{\cdot}002$ and $P=0{\cdot}033$, respectively). It may be that the hopanols are mainly derived from a distinct bacterial group such as cyanobacteria, which have been found to be enriched in this compound class (Rohmer *et al.*, 1984; Summons *et al.*, 1999), and may be similarly distributed in space and time as dinoflagellates. Most algal lipid biomarker compounds are significantly intercorrelated.

The compounds shown in Figure 3 are representative of the range of sources of OM to CB. Despite considerable variation due to spatial and temporal factors, a few patterns emerge. The average relative abundance of 29Δ5, LCFA and 24OH, all likely

TABLE 2. Lipid compound abbreviations and source assignments used in this study. Assignments are dominant but not exclusive to the sources indicated

Compound group or compound	Abbreviation	Major source (reference‡)
Σ fatty acids (FA)	ΣFA*	non-specific
Σ C_{22} & Σ C_{20} polyunsaturated FA	22PUFA, 20PUFA	algae (Killops & Killops, 1993; Volkman, 1986), zooplankton (Lee *et al.*, 1971)
Σ C_{18} & Σ C_{16} polyunsaturated FA	18PUFA, 16PUFA	algae, diatoms tend to have more 16PUFA relative to non-diatom algae 18PUFA (Volkman *et al.*, 1989).
Σ C_{18} & C_{16} monounsaturated FA	18 MUFA, 16MUFA	algae (Killops & Killops, 1993; Volkman, 1986), zooplankton (Lee *et al.*, 1971), bacteria (Gillian & Johns,1986)
Σ polyunsaturated FA	PUFA	labile ' fresh ' organic matter (Shaw & Johns, 1985)
C_{15}+C_{17} branched FA	15,17Br	bacteria (Parkes & Taylor, 1983; Edlund *et al.*, 1985; Kaneda, 1991)
10 methyl- C_{16} branched FA	10MeBr	bacteria (Parkes & Taylor, 1983; Edlund *et al.*, 1985; Kaneda, 1991)
Σ branched FA	BrFA	general bacteria indicator
Σ long even FA C_{24}-C_{28}	LCFA	higher plants (Cranwell, 1982; Nichols *et al.*, 1982; Reiley *et al.*, 1991)
16:1ω7	16:1ω7	mainly diatoms and cyanobacteria (Moreno *et al.*, 1979; Volkman *et al.*, 1989; Demott *et al.*, 1997)
20:5ω3	20:5ω3	mainly diatoms (Volkman *et al.*, 1989; Viso & Marty, 1993)
22:6ω3	22:6ω3	mainly dinoflagellates (Nichols *et al.*, 1984), low levels in other algae (Volkman *et al*, 1989)
Σ sterols	ΣST†	non-specific
cholesta-5,22-dien-3*β*-ol	27Δ5,22	zooplankton and diatom (Volkman, 1986)
cholest-5-en-3*β*-ol	27Δ5	zooplankton (Volkman, 1986; Killops & Killops, 1993)
24-methylcholesta-5,22-dien-3*β*-ol	28Δ5,22	phytoplankton (Gillian *et al.*, 1981; Volkman, 1986), cyanobacteria (Paoletti *et al.*, 1976)
24-methylcholesta-5,24(28)-dien-3*β*-ol	28Δ5,24(28)	phytoplankton, mainly diatom (Gillian *et al.*, 1981; Volkman, 1986)
24-methylcholest-5-en-3*β*-ol	28Δ5	higher plant and rarely algal (Volkman, 1986)
24-ethylcholesta-5,22-dien-3*β*-ol	29Δ5,22	higher plants (Nichols *et al.*, 1982; Volkman, 1986), cyanobacteria (Paoletti *et al.*, 1976)
24-ethylcholest-5-en-3*β*-ol	29Δ5	higher plants (Nichols *et al.*, 1982; Killops & Killops, 1983), cyanobacteria (Paoletti *et al.*, 1976); freshwater microalgae (Volkman *et al.*, 1999)
24-ethylcholesta-5,24(28)-dien-3*β*-ol	29Δ5,24(28)	algal (Volkman, 1986), diatom (Volkman & Hallegraeff 1988)
4α,23,24-trimethylcholest-22-en-3*β*-ol	30Δ22	dinoflagellates (Boon *et al.*, 1979; Nichols *et al.*, 1984; Volkman *et al.*, 1989)
4α,23,24-trimethyl-5α(H)-cholestan-3*β*-ol	30Δ0	dinoflagellates (Nichols *et al.*, 1984)
C_{24} Alcohol	24OH	higher plants (Cranwell, 1982; Reiley *et al.*, 1991)
Σ Hopanols	ΣHOP	bacteria including cyanobacteria (Ourisson *et al.*, 1979; Cranwell, 1982; Rohmer *et al.*, 1984)

*Fatty acids are designated as A:BωC 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 end of the molecule.
†Sterol abreviated as AΔX,Y where A refers to the number of carbon atoms and ΔX,Y refers to the position of double bonds following the ring numbering system for steroids (Killops and Killops, 1993).
‡Compounds are predominant in, but not exclusive to, the sources listed. Algal monoculture data in Zimmerman, 2000 serve as an additional reference for source assignments.

TABLE 3. Concentration of total fatty acid (ΣFA) expressed relative to mass dry weight sediment and carbon content of sediment and relative abundance (percent total fatty acid) of selected fatty acids present in surface sediments

Spl.#*	ΣFA† $\mu g/g^{-1}$ sed	ΣFA µg/mgC	BrFA	C_{22} PUFA	C_{20} PUFA	C_{18} PUFA	C_{16} PUFA	C_{18} MUFA	C_{16} MUFA	15,17Br	10MeBr	LCFA	16:1ω7	20:5ω3	22:6ω3
1	49·3	3·7	8·19	1·87	0·96	0·59	0·39	23·77	17·37	6·26	0·00	6·19	14·91	0·00	1·87
2	83·1	5·3	8·09	0·88	1·74	1·14	1·90	26·13	21·19	5·23	0·46	4·31	18·68	1·29	0·88
3	67·0	2·2	9·00	0·21	2·20	4·37	0·92	17·75	18·47	6·09	0·66	6·90	14·93	1·62	0·21
4	82·8	5·2	7·36	2·89	4·89	2·09	0·84	19·23	20·67	3·97	0·40	3·73	18·40	4·30	1·80
5	32·2	0·8	12·93	2·70	1·77	0·53	0·58	8·25	2·25	6·90	0·83	12·10	1·83	1·02	0·90
6	135·0	2·7	13·88	3·10	5·30	2·24	0·97	17·12	16·48	8·49	1·50	4·10	13·33	5·07	0·47
7	133·8	3·5	10·79	5·84	8·56	1·64	0·79	19·93	12·21	6·35	1·25	4·33	9·34	7·62	1·12
8	61·2	2·0	6·66	7·66	5·92	1·78	0·84	15·27	15·00	2·14	0·12	4·14	10·48	4·29	0·28
9	92·0	2·8	13·11	3·58	6·15	1·97	0·90	14·52	13·36	8·75	0·17	4·56	9·74	4·42	0·52
10	341·2	9·1	7·29	1·81	4·54	0·00	0·69	17·60	25·05	4·97	0·00	2·05	23·02	3·19	0·82
11	873·3	23·8	4·48	5·17	10·13	4·39	2·23	7·60	33·04	1·57	0·37	0·81	32·18	9·38	1·55
12	164·2	5·5	7·38	0·76	2·09	3·86	0·00	13·41	23·08	5·15	0·71	4·88	21·41	2·09	0·76
13	351·8	10·2	9·04	4·91	4·94	4·26	0·81	14·45	23·34	5·96	0·74	2·25	21·56	4·20	3·44
14	267·9	8·3	7·67	1·41	4·86	3·25	0·99	10·43	23·73	5·04	0·69	2·43	22·32	4·51	0·00
15	469·1	12·0	5·61	1·41	2·47	1·81	0·00	15·14	19·23	3·75	0·51	0·68	17·17	1·51	1·00
16	648·3	16·7	5·24	4·08	6·15	2·86	0·00	18·61	16·82	3·81	0·55	0·61	15·70	2·86	2·83
17	642·3	15·5	10·16	0·22	1·97	0·68	0·35	6·33	21·18	5·80	1·50	3·35	21·18	1·06	0·22
18	547·4	14·6	6·32	1·63	3·10	2·89	0·42	17·02	19·09	4·11	0·64	1·39	17·73	2·53	1·17
19	403·9	11·1	7·80	3·35	4·71	2·87	0·55	14·55	16·56	5·59	0·71	1·83	15·21	4·11	1·92
20	136·2	4·2	10·68	1·20	3·14	2·55	0·00	18·39	24·77	7·04	1·55	2·74	22·54	3·14	0·00
21	433·0	17·9	4·73	3·40	9·42	4·60	1·20	10·82	37·07	2·25	0·34	0·74	35·77	8·58	0·41
22	388·2	12·7	4·56	2·56	4·59	4·47	0·20	13·49	34·44	3·46	0·32	1·35	33·07	3·62	1·21
23	303·4	9·9	7·57	0·95	3·93	3·16	1·17	14·39	23·32	5·42	0·76	10·24	21·74	2·96	0·00
24	478·2	13·9	6·87	6·41	2·96	2·80	0·56	22·49	18·90	4·77	0·23	1·82	17·65	2·21	5·60
25	285·9	12·3	10·40	5·55	5·25	2·52	0·71	14·42	22·85	6·42	1·18	0·00	21·93	5·25	3·27

TABLE 3. *Continued*

Spl.#*	ΣFA† $\mu g/g^{-1}$ sed	ΣFA µg/mgC	BrFA	C_{22} PUFA	C_{20} PUFA	C_{18} PUFA	C_{16} PUFA	C_{18} MUFA	C_{16} MUFA	15,17Br	10MeBr	LCFA	16:1ω7	20:5ω3	22:6ω3
25	285·9	12·3	10·40	5·55	5·25	2·52	0·71	14·42	22·85	6·42	1·18	0·00	21·93	5·25	3·27
26	282·2	11·8	22·14	2·77	0·99	2·82	0·00	15·74	18·28	13·05	1·54	1·01	16·73	0·99	1·46
27	263·4	10·5	19·21	1·84	0·88	1·93	0·00	17·12	17·91	12·95	1·89	1·07	16·47	0·88	0·99
28	344·3	14·3	19·87	0·00	0·98	2·36	0·00	14·37	24·63	9·14	1·56	0·58	23·18	0·98	0·00
29	492·6	17·7	5·15	1·77	4·03	2·32	0·59	9·01	36·55	3·14	0·32	0·53	35·43	3·32	0·53
30	617·8	19·3	5·73	2·37	3·41	2·30	0·61	14·72	24·32	3·80	0·38	4·18	23·00	2·77	1·01
31	379·2	13·1	6·50	1·72	1·89	1·74	0·60	18·22	17·45	4·39	0·52	3·34	16·23	1·16	1·47
32	284·4	9·8	8·46	1·76	1·81	1·32	0·30	14·08	16·40	5·92	0·66	1·70	15·06	1·42	1·36
33	351·9	11·6	6·68	7·70	1·92	0·00	0·27	14·20	14·92	4·26	0·49	1·72	13·82	1·50	0·00
34	300·1	11·9	4·73	4·38	5·57	2·77	0·00	14·67	18·48	3·27	0·00	1·22	17·29	4·96	1·21
35	265·6	10·1	7·27	1·78	0·62	1·20	0·00	19·28	11·43	5·30	0·70	1·30	10·12	0·62	0·86
36	68·8	12·1	14·24	2·39	8·20	3·00	0·91	12·40	23·18	10·02	1·36	0·00	22·16	7·83	2·39
37	37·5	6·3	19·11	0·35	1·16	2·29	0·00	15·50	18·04	15·13	0·00	0·00	16·62	1·16	0·35
38	24·8	5·8	14·84	2·90	1·30	1·11	0·00	15·93	21·47	9·72	1·90	0·00	21·47	1·30	1·61
39	70·6	6·9	8·97	3·91	0·39	3·16	0·00	23·37	1·07	3·96	0·00	0·00	0·00	0·00	3·42
40	16·0	8·5	14·17	6·79	7·14	1·58	0·80	15·94	15·24	9·04	1·82	1·31	13·91	6·93	0·50
41	104·1	35·7	7·89	6·79	16·97	0·83	3·02	8·89	24·71	2·99	0·48	0·30	0·00	16·69	1·07
42	126·8	31·4	9·68	7·32	14·02	1·87	1·74	9·69	23·28	5·63	0·55	0·49	22·34	13·42	0·31
43	21·7	8·1	13·81	4·87	9·08	1·45	1·01	6·45	18·16	8·78	1·52	1·43	16·81	8·67	0·67
44	25·6	8·0	17·53	3·62	7·73	1·68	1·87	6·70	16·49	10·33	1·79	1·29	14·95	7·13	0·51
45	12·2	5·2	10·54	0·00	1·08	1·31	0·00	17·07	20·84	8·05	1·54	1·05	18·97	1·08	0·00
46	93·5	25·5	4·60	3·76	6·56	3·42	0·93	9·67	32·21	2·13	0·40	0·73	31·29	5·90	2·07
47	28·4	16·9	6·34	2·46	5·33	3·85	0·33	13·28	24·91	4·83	0·35	0·44	23·68	4·46	0·78
48	14·0	6·2	7·85	1·99	2·11	2·00	0·00	20·42	19·72	5·78	1·26	1·11	18·29	2·11	1·99
49	29·9	6·9	8·71	7·75	2·54	0·86	0·30	18·77	17·73	5·88	0·86	2·18	16·10	2·54	7·12

*Sample numbers correspond to those in Table 1.
†Compound and compound group abbreviations are listed in Table 2.

TABLE 4. Concentration of total sterol (Σ ΣST) expressed relative to mass dry weight sediment and carbon content of sediment and relative abundance (percent total sterols) of selected sterols present in surface sediments.

Spl.#*	ΣST† μg/g^{-1} sed	ΣST μg/mgC	27Δ5,22	27Δ5	28Δ5,22	28Δ5, 24(28)	28Δ5	29Δ5,22	29Δ5	29Δ5, 24(28)	30Δ22	30Δ0	24OH	ΣHOP
1	20·5	0·81	1·96	11·78	6·48	5·65	9·11	8·27	17·03	0·00	2·32	0·00	2·61	2·41
2	12·9	0·44	7·70	22·42	6·71	8·71	6·75	7·40	24·68	0·00	0·00	0·00	1·58	0·00
3	27·5	0·48	3·30	18·09	6·90	7·83	0·81	7·18	24·94	0·58	1·72	0·00	0·00	1·26
4	24·7	0·82	2·47	17·17	7·93	16·87	7·41	5·35	19·33	1·19	1·10	0·00	0·00	0·00
5	28·6	0·39	3·18	15·05	6·29	4·35	7·84	5·79	12·87	0·00	4·84	1·32	6·88	4·43
6	43·6	0·46	2·28	15·76	4·99	4·31	4·23	5·93	0·00	6·78	4·51	0·94	8·02	2·96
7	90·1	1·23	3·13	24·40	6·32	5·54	5·21	0·00	0·00	4·90	2·63	0·81	7·08	2·67
8	22·3	0·38	2·57	15·02	5·33	5·42	5·96	5·54	16·12	0·00	3·54	0·99	7·43	4·14
9	30·2	0·48	3·20	16·35	5·62	4·53	5·92	5·47	18·91	0·00	3·22	0·94	6·21	3·49
10	212·3	2·97	2·83	9·86	8·15	6·05	5·77	8·37	11·94	1·88	9·49	1·70	0·00	3·67
11	152·2	2·18	5·23	14·55	7·51	19·95	4·25	3·39	11·86	4·00	4·86	1·06	0·44	2·82
12	100·9	1·78	3·21	13·16	7·12	9·64	4·74	5·80	16·72	2·07	6·16	1·10	0·00	3·17
13	220·9	3·37	5·29	15·86	13·71	8·90	5·05	3·91	8·15	2·72	4·17	0·50	0·00	1·86
14	154·2	2·50	3·64	12·51	7·65	7·41	7·32	4·99	13·74	1·90	6·62	1·04	0·00	3·59
15	183·1	2·47	3·40	14·70	8·71	7·66	5·84	0·75	11·15	2·05	7·90	1·10	0·00	4·51
16	232·7	3·15	3·25	8·86	7·77	6·66	5·80	6·86	11·61	2·55	8·41	1·54	0·00	6·22
17	273·9	3·48	4·04	13·66	9·55	13·41	5·80	5·15	11·08	2·89	8·89	1·75	1·42	2·00
18	197·3	2·77	3·45	10·71	9·77	10·46	6·36	5·59	10·30	3·23	7·33	1·17	0·00	3·38
19	252·7	3·66	2·66	10·46	7·71	8·68	8·78	5·21	11·51	2·86	9·01	2·15	0·00	3·09
20	108·6	1·78	3·95	8·45	7·48	5·70	5·11	6·26	3·02	1·37	6·46	1·38	0·00	9·85
21	112·7	2·45	4·88	12·86	12·60	12·90	4·61	5·00	10·90	3·93	4·17	0·83	0·00	5·58
22	158·6	2·73	4·89	15·15	10·64	14·83	4·23	4·39	1·56	4·65	5·48	1·09	0·00	3·65
23	276·2	4·73	2·87	9·20	6·61	28·73	6·13	3·85	9·88	9·23	4·01	0·68	0·00	2·89
24	199·1	3·05	4·21	12·69	7·50	8·62	7·29	6·68	11·20	2·51	5·65	1·18	0·00	5·23
25	77·2	1·74	4·48	10·71	9·24	9·49	10·54	4·56	11·48	5·03	6·08	1·29	0·00	2·11

TABLE 4. *Continued*

Spl.#*	ΣST† μg g^{-1} sed	ΣST μg mgC	27Δ5,22	27Δ5	28Δ5,22	28Δ5, 24(28)	28Δ5	29Δ5,22	29Δ5	29Δ5, 24(28)	30Δ22	30Δ0	24OH	ΣHOP
26	84·8	1·87	4·14	12·49	8·64	7·99	7·73	4·86	8·20	2·50	4·02	1·44	0·00	3·14
27	77·6	1·63	5·38	12·21	8·08	6·16	7·57	4·41	7·50	1·60	6·72	2·87	0·00	3·28
28	92·9	2·04	5·33	21·19	9·63	6·31	7·03	3·69	6·33	1·58	5·46	2·12	0·00	2·38
29	103·1	1·95	4·63	13·69	12·62	13·40	5·79	4·40	10·77	3·48	4·36	0·83	0·00	3·95
30	224·0	3·69	3·67	13·29	7·46	12·83	13·62	4·25	9·39	6·67	4·64	0·80	0·00	2·99
31	156·1	2·84	3·40	9·79	7·55	21·32	7·65	4·36	10·19	6·48	4·98	0·92	0·39	3·12
32	125·9	2·28	5·24	13·24	8·21	7·39	6·59	7·12	10·88	2·16	4·38	0·94	0·00	3·92
33	113·7	1·97	4·71	12·76	9·14	7·18	5·53	6·93	10·17	2·34	5·27	1·28	0·00	4·63
34	71·0	1·48	6·17	20·63	9·03	12·34	4·33	4·93	7·30	2·06	4·54	0·94	0·00	4·25
35	72·3	1·45	5·98	11·62	7·97	8·38	6·09	6·20	10·35	2·61	5·05	1·07	0·00	4·41
36	16·8	1·56	5·74	24·24	10·63	13·49	5·36	3·76	8·77	4·65	3·94	1·08	0·00	1·15
37	9·3	0·83	5·98	18·82	9·67	4·91	5·52	4·66	8·77	0·00	5·72	2·01	0·00	2·50
38	8·0	0·99	6·57	16·76	8·03	6·71	7·54	4·30	8·35	1·58	7·56	0·00	0·00	3·34
39	31·5	1·63	5·47	17·01	5·81	20·94	6·40	2·26	10·97	4·88	4·94	1·19	0·00	1·27
40	3·7	1·03	5·29	14·76	8·87	6·91	5·58	4·98	9·35	1·79	4·67	1·58	2·47	2·35
41	11·4	2·05	4·96	0·16	9·30	10·67	5·15	2·84	10·47	3·01	4·35	0·93	2·41	1·27
42	17·7	2·31	4·59	20·49	9·82	11·84	4·41	4·93	11·50	4·81	3·88	0·81	1·16	1·26
43	8·4	1·63	4·71	0·00	10·01	12·16	4·43	5·01	11·65	4·90	3·96	0·85	1·17	1·35
44	8·3	1·38	5·20	16·40	8·19	5·97	5·24	4·98	10·09	2·14	5·04	1·32	1·67	2·37
45	5·0	1·14	5·13	15·35	9·17	6·92	7·34	5·29	9·74	2·02	5·03	1·54	1·43	5·26
46	13·1	1·89	5·25	13·71	10·31	11·39	5·39	3·49	12·94	2·83	6·27	1·03	1·30	2·97
47	6·4	1·99	4·78	17·35	11·17	10·20	4·00	5·43	12·18	5·29	4·80	0·99	0·00	2·22
48	6·8	1·57	4·99	17·43	9·70	7·96	4·87	5·13	9·21	1·71	5·60	1·35	1·42	4·61
49	15·4	1·87	5·28	17·14	9·73	6·87	5·75	4·76	9·17	2·24	5·60	1·32	0·94	4·64

*Sample numbers correspond to those in Table 1.
†Compound and compound group abbreviations are listed in Table 2.

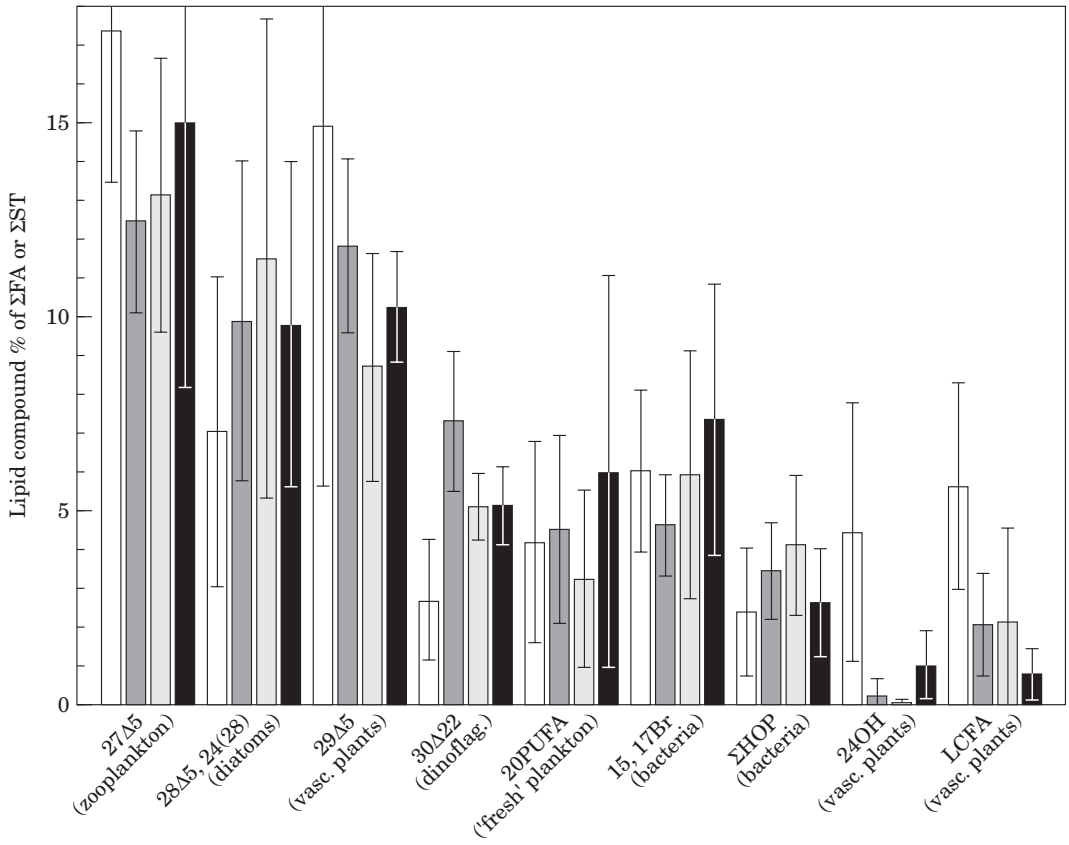

FIGURE 3. Regional means of selected biomarker concentrations in CB surface sediments (percent sterol relative to total sterols and percent fatty acid relative to total FA). Error bars represent standard deviation from the mean. Data from all seasons are included. Compound abbreviations and dominant source assignment references are listed in Table 2. □ Northern Bay (n=9), ▩ Upper Mid-Bay (n=10), ▨ Lower Mid-Bay (n=16), ■ Southern Bay (n=14).

derived from higher plants, tends to be greatest in the North Bay (Figure 3). Many of the algal biomarkers (e.g. 28Δ5,24(28) and 30Δ22) are enriched in the Mid-Bay and South Bay regions. However, seasonal trends in the relative percent abundance of most of the biomarker compounds were not apparent due to the high degree of variability within each season. Despite this variability, 20PUFA, 18PUFA and 16MUFA were enriched, on average, in spring samples and 28Δ5,24(28) and 29Δ5,24(28) were enriched in spring and summer samples (Tables 3 and 4). Although graphical analysis of regional and seasonal means of biomarker concentrations is informative, its usefulness is limited by the high degree of spatial and temporal variability in surficial sediment OM composition.

Principal components analysis

Principal components analysis was carried out in an effort to reduce the complexity of the data and to discern geochemical trends. Principal components analysis was applied to the weight percent normalized data matrix of 27 variables (those listed in Table 2 except ΣFA and ΣST) and 49 observations (samples). We found the PCA model to be robust in that similar results were obtained when the number and type of variables used or the normalization procedure was altered. Further, Q-mode factor analysis produced similar results. Although each of the first three principal components (PCs) explain more of the variance in the data than any of the variables alone (eigenvalues of 6·1, 3·9, and 3·4, respectively), they only account for 24, 15 and 13% of the total variance in the data, respectively. A good deal of the variability is left unaccounted for which attests to the large number of factors that contribute to the high variability of OM composition in this system. However, these three PCs, which together represent 52% of the variability, do appear to represent geochemically interpretable factors.

Variable loadings. Factor coefficients (or loadings) are correlation coefficients between each variable and

each PC. Positive loadings indicate a direct relationship and those variables with the greatest absolute magnitude exert the greatest influence on the PC. By plotting the variable loadings of PC1 versus PC2 [Table 5(a); Figure 4(a)] a geochemical interpretation of the underlying causes of variance in the data can be made. Biomarkers with similar geochemical associations project close to one another in the PC coordinate space. Principal component 1 is most negatively loaded [loading $< -0{\cdot}2$: bold font in Table 5(a)] on polyunsaturated FA, primarily of ' fresh ' algal origin. The strong loadings on total PUFA, 16PUFA, 20PUFA and 22PUFA indicate that PC1 also represents an aspect of OM lability as these groups are readily degraded and/or utilized by heterotrophic organisms. Negative loadings on PC1 may also indicate relatively greater OM contributions from diatoms as compounds such as 16PUFA relative to 18PUFA and 16MUFA relative to 18MUFA that are derived from diatoms (Volkman *et al.*, 1989; Zimmerman, 2000) tend to be more negatively loaded on PC1. Compounds with positive loadings on PC1 (quadrants I and II) are of mixed origin (i.e. terrestrial, zooplankton, dinoflagellate and bacterial) and tend to be more geochemically stable than the negatively loaded compounds.

Principal component 2 is most positively loaded (loading $>0{\cdot}2$) on 24OH and LCFA, terrestrial-source indicators [Figure 4; Table 5(a)]. Though not as heavily loaded, sitosterol (29Δ5), campesterol (28Δ5) and stigmasterol (29Δ5,22) also plot in quadrant I. This may indicate at least a partial terrestrial origin for these compounds. Most of the PUFAs also have positive PC2 loadings suggesting that although their origin is likely autochthonous (i.e. diatoms), their distribution may be influenced by external processes (e.g. freshwater inflow that enhances stratification and nutrient delivery). Compounds with negative loadings on PC2 are of mixed algal origin. 18PUFA and 16:1ω7, for example, are enriched in both diatom and non-diatom algae. Again, a close association between hopanol (possibly of cyanobacterial origin) and dinoflagellate sterols (30Δ0, 30Δ22) is indicated.

Principal component 3 is most heavily loaded on the bacterial OM indicators 15,17 Br, 10 MeBr and ΣBrFA [loadings of 0·38, 0·39 and 0·41, respectively; Table 5(a)]. The stanol 30Δ0 is also highly loaded on PC3. This compound can be formed by the microbially mediated reduction of sterols that often occurs at oxic-anoxic boundaries in the water column (Wakeham, 1989). However, 30Δ0 has also been shown to occur in some plankton including a freshwater dinoflagellate (Robinson *et al.*, 1984). The strong PC3 association with 30Δ0 as well as the positive correlation between 30Δ0 and 15,17 Br, 10 MeBr ($P=0{\cdot}009$ and $P=0{\cdot}042$, respectively) suggest that PC3 may be a component representative of OM deposited from an anoxic or hypoxic water column or derived from anaerobic bacteria present in sediments underlying these regions. These PC interpretations may be corroborated through an examination of the PC scores on each of the samples in the data set.

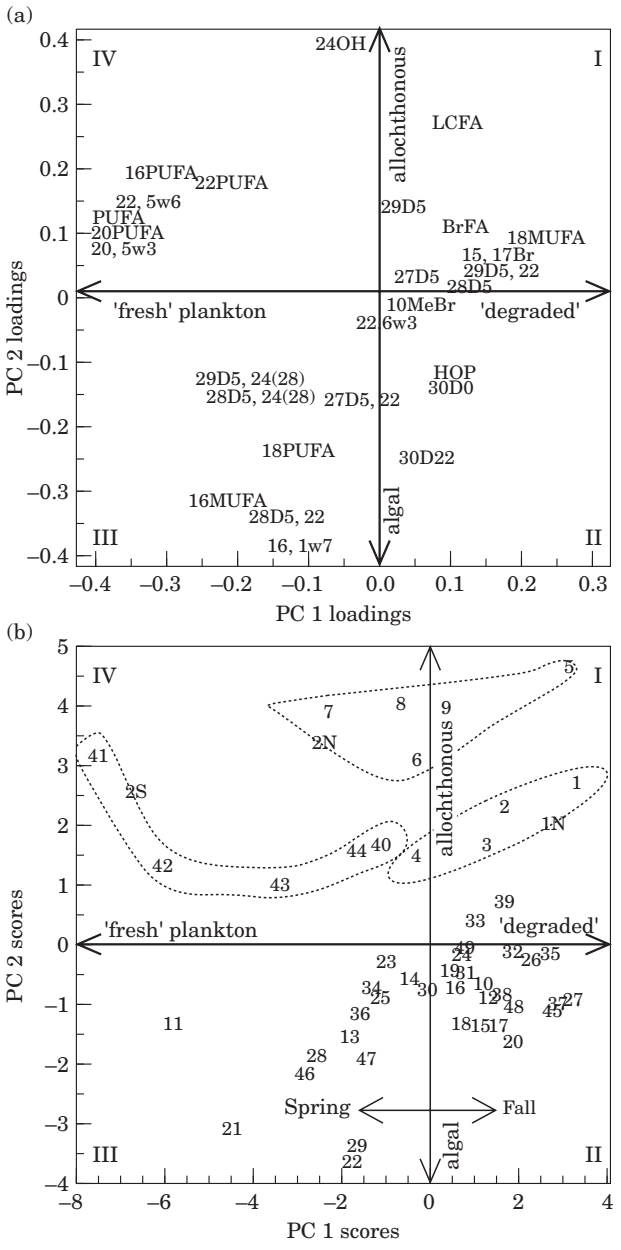

FIGURE 4. Plot of (a) variable factor coefficients (loadings; abbreviations used for variables are given in Table 2) and (b); sample scores (observation numbers correspond to sample numbers listed in Table 1) for the first two principal components identified by PCA.

TABLE 5. PCA variable loadings and sample scores

(a) Variables	Loadings* PC1	PC2	PC3	(b) spl#2	Site	Scores PC1	PC2	PC3	Scores spl#†	Site	PC1	PC2	PC3
PUFA	**−0·38**	0·12	0·08	1	1N	3·40	2·77	−3·32	**26**	2LM	2·35	−0·23	2·72
BrFA	0·12	0·11	**0·41**	2	1N	1·78	2·28	−3·37	27	2LM	3·25	−0·95	4·15
22PUFA	**−0·22**	0·18	0·08	3	1N	1·43	1·69	−3·51	28	2LM	−2·48	−1·90	2·94
20PUFA	**−0·38**	0·10	0·08	4	1N	−0·23	1·51	−3·37	29	2LM	−1·56	−3·39	−1·38
18PUFA	−0·12	**−0·24**	−0·13	5	2N	3·11	4·67	0·26	**30**	2LM	0·03	−0·70	−1·69
16PUFA	**−0·30**	0·19	−0·06	6	2N	−0·23	3·10	1·77	**31**	2LM	0·83	−0·47	−1·95
18MUFA	**0·22**	0·09	−0·15	7	2N	−2·23	3·94	2·15	32	2LM	1·93	−0·13	−0·44
16MUFA	−0·20	**−0·34**	−0·09	**8**	2N	−0·58	4·06	−1·34	33	2LM	1·05	0·39	−0·05
15,17Br	0·16	0·06	**0·38**	9	2N	0·44	4·02	−0·21	34	2LM	−1·25	−0·67	−0·61
10MeBr	0·06	0·00	**0·39**	10	2UM	1·29	−0·68	−0·67	**35**	2LM	2·75	−0·17	−0·35
LCFA	0·10	**0·27**	**−0·22**	11	2UM	−5·71	−1·30	−1·24	36	1S	−1·49	−1·15	1·70
16:1ω7	−0·10	**−0·39**	−0·09	12	2UM	1·45	−0·83	−1·74	**37**	1S	2·99	−1·01	2·64
20:5ω3	**−0·38**	0·09	0·11	**13**	2UM	−1·69	−1·52	−0·12	38	1S	1·69	−0·81	2·03
22:6ω3	0·01	−0·04	−0·05	14	2UM	−0·32	−0·60	−0·60	39	1S	1·76	0·72	−1·22
27Δ5,22	−0·03	−0·16	0·16	15	4UM	1·18	−1·36	−0·25	40	2S	−1·06	1·63	2·96
27Δ5	0·06	0·03	0·01	16	4UM	0·62	−0·76	−0·40	41	2S	−7·55	3·12	1·35
28Δ5,22	−0·14	**−0·34**	0·09	17	4UM	1·59	−1·40	0·90	42	2S	−6·01	1·31	0·97
28Δ5,24(28)	−0·15	−0·15	**−0·23**	**18**	4UM	0·79	−1·35	−0·83	**43**	2S	−3·32	0·94	1·98
28Δ5	0·13	0·01	0·00	19	4UM	0·50	−0·46	0·47	44	2S	−1·62	1·58	3·28
29Δ5,22	0·16	0·05	−0·16	20	1LM	1·96	−1·64	1·34	45	3S	2·87	−1·10	1·15
29Δ5	0·04	0·14	**−0·33**	21	1LM	−4·39	−3·06	−1·25	46	3S	−2·71	−2·17	−0·96
29Δ5,24(28)	−0·18	−0·13	−0·02	22	1LM	−1·69	−3·67	−0·93	47	3S	−1·35	−1·91	−0·81
30Δ22	0·07	**−0·25**	0·18	**23**	1LM	−0·97	−0·31	−2·76	**48**	3S	1·93	−1·05	0·36
30Δ0	0·10	−0·14	**0·34**	24	1LM	0·81	−0·16	−1·26	49	3S	0·86	−0·05	0·58
24OH	−0·03	**0·40**	0·08	25	2LM	−1·12	−0·78	0·92					
ΣHOP	0·11	−0·14	0·05										

*Loadings greater than |0·2| are indicated in bold face.
†Spring samples are underlined, summer samples are in bold face.

Observation scores. The PC scores indicate the relative influence of each PC on the sample composition. Nearly all fall samplings have positive PC1 scores while spring samplings tend to have negative PC1 scores [Table 5(b); Figure 4(b)]. Of the seven samples with the most negative PC1 scores (quadrants III and IV), six were collected in the spring of 1996 and four were collected in March 1996 coincident with the spring bloom and the predominance of diatoms and/or labile OM production. The seasonal progression from diatom to non-diatom and/or labile to more refractory OM can most clearly be seen in the score plots of sites 1N, 2N and 2S that, moving from left to right, progress from spring to summer to fall samplings.

All of the samples from sites 1N (#1–4), 2N (#5–9) and 2S (#40–44) have positive scores for PC2 [Table 5(b)] indicating that these locations are most influenced by allochthonous OM sources or processes external to the Bay proper [Figure 4(b)]. Most samples from all other sites have negative PC2 scores suggesting that they are dominated by autochthonous OM inputs.

Some of the samples with the highest PC3 scores were those of the Mid-Bay collected during the summer [Table 5(b)] when one would expect bacterially-derived OM contribution to be greatest because bacterial production is the highest at this time (Shiah & Ducklow, 1994). However, no correlation was found between samples with high PC3 scores and low bottom water oxygen concentration, and samples with high PC3 scores can be found in all regions of the Bay during all seasons. These sample score distributions appear to validate the interpretation of these PCs as indicators of OM source and lability and their ability to represent both spatial and temporal variations in surficial sediment OM composition.

Discussion

Spatial variation of organic matter composition

As has been found in other studies (Canuel & Zimmerman, 1999; Harvey & Johnston, 1995), the OM in CB sediments is mainly autochthonous in origin, predominantly derived from a mixture of phytoplankton, zooplankton and bacteria. However, stable isotope and lipid analyses reveal substantial spatial variability in the distributions of these autochthonous OM sources as well as a contribution of allochthonous OM to certain regions of the Bay. PC2, with its positive loadings on compounds derived from higher plants and negative loadings on algal markers, clearly represents this spatial variability. Though PC2 scores were correlated with $\delta^{13}C$ ($r = -0{\cdot}40$, $P = 0{\cdot}009$) and $\delta^{15}N$ ($r = -0{\cdot}58$, $P < 0{\cdot}001$), they were best correlated with $C{:}N_a$ ($r = 0{\cdot}73$, $P < 0{\cdot}0005$). Site 2N in the North Bay, with the highest PC2 scores and $C{:}N_a$ and the most depleted $\delta^{13}C$ and $\delta^{15}N$ signatures, is clearly a site of terrestrial OM deposition. Site 1N, just north of 2N, has an even more depleted $\delta^{13}C$ signature [Figure 2(c)] but also slightly lower PC2 scores and $C{:}N_a$ (indicating less terrestrial OM influence). We can hypothesize that differences in the hydrodynamics and bathymetry of these two sites (as supported by the much lower surface area and TOC content at 1N) contribute to the observed differences in the amount and type of terrestrial OM deposited at these proximal sites.

Site 2S also had high PC2 scores but does not have stable isotope or $C{:}N_a$ signatures indicative of vascular plant input. It has low sediment surface area and TOC content but relatively high contributions of labile algal-derived material (negative PC1 scores and high PUFA content). A possible explanation is that this site receives OM with ^{13}C-enriched carbon (e.g. seagrasses and C4 plants like the marsh macrophyte *Spartina* spp. or from benthic diatoms; $\delta^{13}C = -12$ to $-13‰$ and $-14{\cdot}9‰$, respectively; Stribling & Cornwell, 1997). Pelagic diatoms too have been shown to have highly enriched ^{13}C signatures under certain conditions (Fry & Wainright, 1991). A macrophyte OM contribution may not be reflected in higher $C{:}N_a$ signatures if it is balanced by a contribution of algal material with very low $C{:}N_a$, possibly living benthic diatoms. The absence of fine grain sediment accumulation may also make 2S a preferred site for benthic diatoms. It has also been shown that a convergent residual eddy persists in the region of site 2S that results in high particulate concentrations and downwelling currents (Hood *et al.*, 1999). Ocean-derived phytoplankton OM may be trapped at this site along with terrestrial OM (possibly from the James R. and York R.) that is often associated with coarse sediments (Prahl *et al.*, 1994). Though there remain a number of explanations, it is clear that sediment OM at site 2S is geochemically distinct.

The distribution of bacterially-derived OM is reflected most clearly in PC3. The sample scores of PC3 are highly correlated with the carbon-normalized concentrations of biomarkers for bacteria, 15,17 Br and 10 MeBr (Kaneda, 1991; $r = 0{\cdot}579$ and $r = 0{\cdot}594$, respectively, $P < 0{\cdot}001$). OM from site 1N, however, has a much lower than expected PC3 score based upon the above relationship indicating that 1N sediment lipid composition is unlike that expected for bacterially-derived OM in CB as whole. This may be due to the absence of sulfate reducing bacteria in these

coarse nearly freshwater sediments of the North Bay or a unique contribution from soil-derived bacterial.

On a weight basis (μg g^{-1}), the distribution of bacterial OM, as indicated by the branched FA and hopanols, is an order of magnitude greater in the Mid-Bay relative to the North or South Bay. As the $\delta^{15}N$ OM signatures were not seasonally variable (and therefore not related to primary productivity), we attribute the maximal $\delta^{15}N$ values of the Mid-Bay to the intense biological processing of OM (i.e. nitrification and denitrification) by the large microbial populations of this region. On a carbon-normalized or relative percent basis, however, the bacterial lipids represent an equal or greater portion of the OM in the South Bay relative to the Mid-Bay (Figure 3). This is also indicated by the high PC3 scores in many South Bay sediments [Table 5(b)]. The sediments of the South Bay likely support a relatively larger microbial population due to a higher proportion of fresh algal OM (indicated by higher PUFA concentrations and PC1 scores). It may be that less degradation occurs prior to deposition in the shallow water column of the South Bay or that the strong tidal circulation of this region provides an additional source of fresh algal material from outside the Bay (see discussion above).

Because none of the PCs clearly and uniquely represent OM derived from non-diatom algal groups, we examined the distribution of 22:6ω3, 30Δ22 and 30Δ0 as indicators of dinoflagellate-derived OM and 18MUFA and 28Δ5 for green flagellate-derived OM. Source assignments were based upon algal monoculture lipid compositions of these algal groups (Zimmerman, 2000) and literature information (Table 2). These dinoflagellate biomarkers are most abundant, both on a mass and relative basis, in Mid-Bay surface sediments, particularly at site 4UM, and the green flagellate marker concentrations were fairly evenly distributed throughout the Bay. While dinoflagellates are more abundant in the higher salinity waters of the Mid- and South Bay, green flagellates have been found to be numerically more important in the North Bay phytoplankton assemblage (Marshall & Alden, 1993; Sellner, 1987). Numerical counts of phytoplankton types in CB (NAS/ODU, 1999) also indicate that during the period of this study, blooms of dinoflagellates occurred mainly in the Mid-Bay and the highest green flagellate abundances were found at North and South Bay locations. It appears that the spatial distribution of water column dinoflagellates is reflected in surface sediment composition while that of the green flagellates is not. Perhaps these smaller-celled algae are more likely to be degraded in the water column or transported out of the Bay rather than deposited to the sediment.

Temporal variation of organic matter composition

PC1 separates lipids of labile OM derived mainly from diatoms from more refractory non-diatom-derived lipids and points to seasonal cycles of algal growth as the dominant mechanism of temporal variability of OM composition in CB. PC1 scores are most strongly correlated with the carbon-normalized concentration of total PUFA ($r = -0{\cdot}82$, $P<0{\cdot}001$) and 20PUFA ($r = -0{\cdot}81$, $P<0{\cdot}001$) as well as individual PUFA compounds derived mainly from diatoms (e.g. 20:5ω3; $r = -0{\cdot}81$, $P<0{\cdot}001$). Of the bulk parameters, PC1 scores are best correlated with surface water chl *a* concentration ($r = -0{\cdot}45$, $P=0{\cdot}001$ for our data; $r = -0{\cdot}43$, $P<0{\cdot}005$ for CBP data). The correlations between PC1 scores and surface water chl *a* are also significant for each region of the Bay examined separately.

The sediments of the Bay as a whole and each region of the Bay receive the most labile algal OM material (as indicated by the highest PUFA concentrations and lowest PC1 scores) during spring. Exceptions are 1N sediments, which had slightly more labile OM during September 1996 and 4UM sediments, which exhibited very little temporal variability in any of the PCs. The sediments of another North Bay site, 2N, were most enriched in labile OM during May and July of 1996. This may reflect the progression of the spring bloom from March in the South Bay to early April in the Mid-Bay to May–June in the North Bay which has been observed via chl *a* measurements (Glibert *et al.*, 1995).

Given the correlation between PC1 scores and surface chl *a* concentration and the coincidence with which these data track the progression of the spring bloom, it appears that the delivery of fresh algal matter to the sediments is both temporally and spatially linked to the spring maximum in phytoplankton biomass. A similar conclusion was reached by Kemp and Boynton (1992) using chl *a* concentration measurements in sediment trap-collected material. Furthermore, the lipid biomarker data support the conclusion that the main agent of this spring sediment compositional change are diatoms which, being larger in cell-size and chain-forming, tend to sink from the surface layer faster than other algal types (Buesseler, 1998).

A lag of roughly one month was observed in the relationship between tributary water volume inflow and the delivery of labile OM (PC1 scores) to the sediments (Figure 5). Other workers have also found

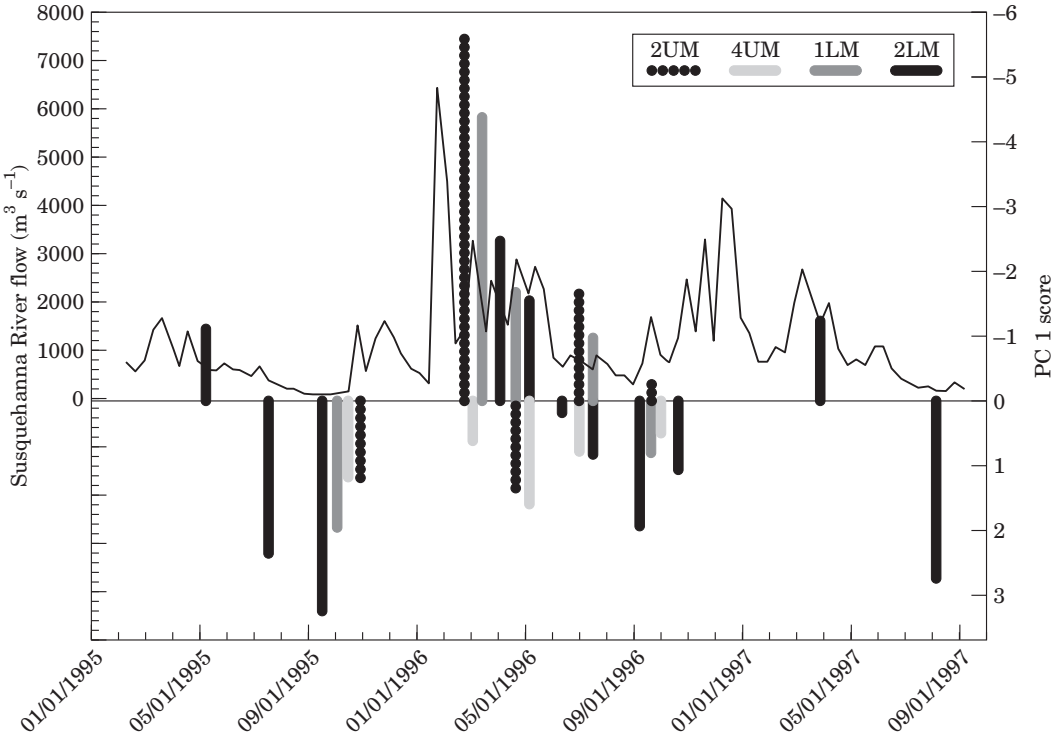

FIGURE 5. Temporal variation of sediment OM composition (PC1 scores) at four Mid-Chesapeake Bay sites and the flow volume record of the Susquehanna River.

correlations between phytoplankton biomass (chl *a* concentrations) in CB and Susquehanna River flow with a 1-month lag (Harding & Perry, 1997; Malone, 1992) though some have not (Fisher *et al.*, 1998). The relationship between water volume and phytoplankton biomass has been attributed both to the delivery of new nutrients to the Bay (Malone *et al.*, 1988) and to the enhancement of water column stratification which decreases the depth of the mixed layer so that phytoplankton receive more light (Pennock, 1985; Sharp *et al.*, 1986).

A component of interannual variability in OM composition is also observed by the comparison of three years of data collected at site 2LM. Sediments from this site exhibit the greatest increase in fresh algal OM delivery (lowest PC1 scores) immediately following the record flows of January–February 1996 relative to the lower flows in 1995 and 1997 (Figure 5). While freshwater inflow and OM compositional changes correspond during this study, we do not have the multi-year or multi-site data to support this general conclusion. It is likely that the timing of water inflow and other factors play additional roles in the dynamics of the spring bloom.

Although sediment OM composition corresponded only vaguely to the spatial distributions of dinoflagellates and green flagellate distributions in the water column, a closer correspondence was found with the reported temporal distributions of these algal groups. While the chlorophytes are often a sub-dominant member of the spring bloom, both of these groups commonly exhibit mid-summer and autumn abundance maxima (Marshall & Alden, 1993; Sellner, 1987). Dinoflagellates are often major portions of the fall phytoplankton assemblage as well (Sellner *et al.*, 1991) and the NAS/ODU data set (NAS/ODU, 1999) indicates dinoflagellate blooms in October/December 1995 and July–October 1996. These blooms occurred mainly in the Mid-Bay and are reflected in the high dinoflagellate biomarker compound concentrations during these times. The highest green flagellate abundances occurred in the Spring of 1996 and between July and October 1996 mainly at North and South Bay locations. These blooms are also reflected in elevated sediment biomarker concentrations for these algae during these times.

In all regions of the Bay, the highest average PC2 score (terrestrially-derived component) was calculated for the fall period. The same was true for PC3 except for the North Bay samples where the highest average score occurred during spring. In general, then, allochthonous and bacteria-derived OM make up the

greatest portion of sediment OM during the fall. This suggests that bacteria preferentially utilize the labile OM deposited during the spring through the summer and fall, converting it to bacterial biomass while more refractory allochthonous OM such as plant material becomes a progressively greater fraction of the remaining material. Fall enrichments in the terrestrial OM component may also be due to increased delivery during the secondary peak in water volume inflow that occurs at this time (Figure 5).

Environmental influences on surface sediment OM composition

The range in phytoplankton biomass, primary productivity, bottom water oxygen and sediment types sampled during this study provide an opportunity to examine the influence of these parameters on surface sediment OM quantity and composition. The close association between TOC and sediment surface area found in the Bay has been noted in other marine and coastal sediments (e.g. Mayer, 1994*a*,*b*; Bergamaschi *et al.*, 1997; Hedges & Keil, 1999) and has been attributed to uniform coatings of OM on mineral surfaces (Mayer, 1994) and the high adsorptive capacities of clays and oxyhydroxides i.e. mineral surface properties (Kaiser & Guggenberger, 2000). In CB, however, the average TOC:surface ratio (slope of TOC versus surface area) is considerably higher ($2{\cdot}5 \pm 1{\cdot}3$ mg TOC m^{-2} surface) than the range of ' organic loadings ' ($0{\cdot}5 - 1$–$1{\cdot}0$ mg TOC m^{-2}) commonly measured in sediments (Mayer, 1994*a*,*b*), is quite variable, and displays no consistent trend. Sediment surface area is not correlated with any of the chemical indicators of OM source (PCA scores or individual biomarkers concentrations). For these reasons, it seems likely that a combination of factors influence the quantity of OM found in surficial sediments including sediment type and hydrodynamics while other factors may be more important in determining sediment OM composition.

Water column DO concentration may play a role in sediment OM composition because without oxygen, respiration cannot be carried out by greater energy-yielding aerobic processes. Benthic organisms, which also consume OM, may become inactive during periods of anoxia/hypoxia (Diaz & Rosenberg, 1995). To establish a connection between oxygenation and OM composition, we looked for correlations between DO and compositional variables (or difference in means) that were present in the whole Bay as well as Mid-Bay-only (the region where anoxia/hypoxia occurs most extensively) data sets. This was necessary to avoid a false conclusion of O_2-influence when other regional factors may be more important. As has been noted, although an inverse DO versus TOC relationship was found for the whole-Bay, this relationship did not hold for the Mid-Bay data set. In fact, no correlations that occurred in both data sets were found between DO and any of the OM parameters. Dinoflagellate biomarker concentrations were greater ($2{\cdot}5\times$) in sediments of the Mid-Bay deposited under anoxic/hypoxic versus oxic water columns but this difference may reflect the predominance of dinoflagellates during the summer when anoxia also occurs rather than a direct influence of DO.

Although some lipid compounds are more susceptible to degradation such as PUFA relative to other FA and most FA relative to sterols (Haddad *et al.*, 1991; Lee *et al.*, 1977), no lipid compounds were significantly enriched (either on a mass, carbon-normalized or relative weight% basis) in sediments of the Mid-Bay sampled under low DO conditions. Thus, we have no evidence that anoxia/hypoxia in CB causes variation in the quantity or composition of OM in surficial sediments. This may not be surprising considering that some have found rates of OM decomposition to be similar for oxic versus anoxic environments (e.g. Henrichs & Reeburgh, 1987; Lee, 1992) and that sediment accumulation rate may be of greater importance in OM preservation (Henrichs & Reeburgh, 1987; Kuehl *et al.*, 1993). Additionally, the periodic nature of bottom water anoxia/hypoxia in CB may not sufficiently inhibit aerobic degradation to affect OM composition. It has been suggested (Aller, 1998) that intermittent anoxia may even promote OM degradation. Seasonal anoxia does, however, permanently alter the benthic community in some portions of CB (Diaz & Rosenberg, 1995) and thus will affect the potential for long-term OM burial.

Conclusions

While graphical examination of lipid compositions in surficial sediments revealed substantial spatial and some temporal variability, PCA was able to distinguish geochemically meaningful components of spatial and temporal variability. This allowed a more complete interpretation of OM distributions and the identification of the dominant mechanisms that explain this variability. Principal component analysis identified three assemblages of sterol and fatty acid biomarkers that, together, represented 53% of the variability in sediment OM composition. Principal component 1, representing the majority of variance in the data (24%), encapsulated much of the seasonal variability in OM composition. It identified algal-derived PUFAs and other lipids derived

predominantly from diatoms as a major influence on the sediment OM composition, particularly during the spring at all but the northernmost sites in the Bay mainstem. The seasonal variation in the distribution of this labile component emphasizes the rapidly changing quality of surface sediment OM.

A second component, representing 15% of the variance in the data described much of the spatial variation in OM composition. With heavy loadings on even-numbered long-chain ($>nC_{22}$) saturated fatty acids and alcohols as well as 24-ethylcholest-5-en-3β-ol (29Δ5), it represents an allochthonously-derived component of sediment OM. Its distribution at the head of the estuary, as well as the stable carbon isotope and $C:N_a$ signatures of these sediments, identify the two northernmost stations as sites of terrestrial OM deposition. This terrestrial component represents the greatest portion of the sediment OM during the fall after algal OM deposited in the spring and summer has been utilized and when tributary flows may be higher. A third component represented bacterially-derived OM was enriched in the South Bay where sediments had the greatest labile component and showed very little seasonal variation in its distribution. Sediment OM composition also reflected the temporal distribution of dinoflagellates and green flagellates in the water column (predominant in the summer) but only the spatial distribution of the former (predominant in the Mid-Bay).

The temporal-variability component of PC1, representing spring diatom-derived OM, was correlated with surface water and water column integrated chl *a* concentration i.e. phytoplankton biomass. There was no evidence to suggest that water column productivity, DO concentration or sediment surface area influenced sediment OM composition, although the latter played a major role in the amount of OM preserved in surficial sediments. These results may at first seem surprising, but when one considers the dynamic physical mixing processes that characterize estuarine circulation, it becomes more unlikely that localized water column conditions will be reflected in underlying sediment. Long-term changes in estuarine-wide parameters such as primary productivity or DO level, however, are more likely to be reflected in the longer sediment record. There is some indication that increased spring freshwater inflows (February 1996) led to greater spring bloom phytoplankton biomass, which translated quickly (March 1996) into increased surface sediment OM lability and a composition enriched in diatom-derived OM. It may be that the algal biomass of the summer is closely coupled in space and time to heterotrophic utilization and therefore does not necessarily become a part of the sediment record. Localized summer algal blooms, however, are less likely to be completely remineralized in the water column and so are reflected in surficial sediment OM composition and, ultimately, the sediment record. In regard to the system as a whole, the estuary appears to act as a trap for terrestrially-derived OM and as a sink for a portion of the OM produced within the estuary.

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References

Aller, R. C. 1998 Mobile deltaic and continental shelf muds as suboxic, fluidized bed reactors. *Marine Chemistry* **61,** 143–155.

Bergamaschi, B. A., Tsamakis, E., Keil, R. G., Eglinton, T. I., Montlucon, D. B. & Hedges, J. I. 1997 The effect of grain size and surface area on organic matter, lignin and carbohydrate concentration and molecular composition in Peru Margin sediments. *Geochimica Cosmochimica Acta* **61,** 1247–1260.

Boon, A. R., Duineveld, G. C. A. & Kok, A. 1999 Benthic organic matter supply and metabolism at depositional and non-depositional areas in the North Sea. *Estuarine, Coastal and Shelf Science* **49,** 747–761.

Boon, J. J., Rijpstra, W. I. C., De Lange, F. & De Leeuw, J. W. 1979 Black Sea sterol—a molecular fossil for dinoflagellate blooms. *Nature* **277,** 125–126.

Buesseler, K. O. 1998 The decoupling of production and particulate export in the surface ocean. *Global Biogeochemical Cycles* **12,** 297–310.

CBP, 2000 Chesapeake Bay Program. (URL) http://www.chesapeakebay.net/data/

Canuel, E. A., Cloern, J. E., Ringelberg, D. B. & Guckert, J. B. 1995 Molecular and isotopes tracers used to examine sources of organic matter and its incorporation into the food webs of San Francisco Bay. *Limnology and Oceanography* **40,** 67–81.

Canuel, E. A. & Martens, C. S. 1993 Seasonal variations in the sources and alteration of organic matter associated with recently-deposited sediments. *Organic Geochemistry* **20,** 563–577.

Canuel, E. A. & Zimmerman, A. R. 1999 Composition of particulate organic matter in the Southern Chesapeake Bay: sources and reactivities. *Estuaries* **22,** 980–994.

Cooper, S. R. & Brush, G. S. 1991 Long-term history of Chesapeake Bay anoxia. *Science* **254,** 992–996.

Cranwell, P. A. 1982. Lipids of aquatic sediments and sedimenting particulates. *Progess in Lipid Research* **21,** 271–308.

Curling, K. & Neilson, B. 1994 Water quality in Chesapeake Bay. Virginia Portion, Water Year 1993 *A Report to Virginia Department of Environmental Quality*, Virginia Institute of Marine Science, Gloucester Point, Virginia.

Dachs, J., Bayona, J. M., Fillaux, J., Saliot, A. & Albaiges, J. 1999 Evaluation of anthropogenic and biogenic inputs into the western Mediterranean using molecular markers. *Marine Chemistry* **65,** 195–210.

Demott, W. R. & Muller-Navarra, D. C. 1997 The importance of highly unsaturated fatty acids in zooplankton nutrition: evidence from experiments with *Daphnia*, a cyanobacterium and lipid emulsions. *Freshwater Biology* **38,** 649–664.

Diaz, R. J. & Rosenberg, R. 1995 Marine benthic hypoxia: a review of its ecological effects and the behaviour responses of benthic macrofauna. *Oceanography and Marine Biology: an Annual Review* **33,** 245–303.

Diaz, R. J. & Schaffner, L. C. 1990 The functional role of estuarine benthos. In: *Perspectives on the Chesapeake Bay, 1990,* (Haire, M. & Krome, E. D., eds). Chesapeake Bay Program, U.S., Environmental Protection Agency.

Eadie, B. J., McKee, B. A., Lansing, M. B., Metz, S. & Trefry, J. H. 1994 Records of nutrient-enhanced coastal ocean productivity in sediments from the Louisiana continental shelf. *Estuaries* **17,** 754–765.

Edlund, A., Nichols, P. D., Roffey, R. & White, D. C. 1985 Extractable and lipopolysaccharide fatty acid and hydroxy acid profiles from *Desulfovibrio* sp. *Journal of Lipid Research* **26,** 982–988.

Fisher, T. R., Hagy, J. D. & Rochelle-Newall, E. 1998 Dissolved and particulate organic carbon in Chesapeake Bay. *Estuaries* **21,** 215–229.

Fisher, T. R., Harding, L. W., Stanley, D. W. & Ward, L. G. 1988 Phytoplankton, nutrients, and turbidity in the Chesapeake, Delaware and Hudson estuaries. *Estuarine, Coastal and Shelf Science* **27,** 61–93.

Fry, B. & Wainright, S. C. 1991 Diatom sources of ^{13}C-rich carbon in marine food webs. *Marine Ecology Progress Series* **76,** 149–157.

Gillan, F. T. & Johns, R. B. 1986 Chemical markers for marine bacteria: fatty acids and pigments. In *Biological Markers in the Sedimentary Record*, (Johns, R. B., ed.). Elsevier, Amsterdam. 364 pp.

Gillan, F. T., McFadden, G. I. & Wetherbee, R. 1981 Sterols and fatty acids from the Antarctic sea ice diatom *Stauroneis amphioxys*. *Phytochemistry* **20,** 1935–1937.

Glibert, P. M., Conley, D. J., Fisher, T. R., Harding Jr., L. W. & Malone, T. C. 1995 Dynamics of the 1990 winter/spring bloom in Chesapeake Bay. *Marine Ecology Progress Series* **122,** 27–43.

Haddad, R.I., Martens, C.S. & Farrington, J.W. 1991 Quantifying early diagenesis of fatty acids in a rapidly accumulating coastal marine sediment. *Advances in Organic Geochemistry* **19,** 205–216.

Harding, L. W. & Perry, E. S. 1997 Long-term increase in phytoplankton biomass in Chesapeake Bay, 1950-1994. *Marine Ecology Progress Series* **157,** 39–52.

Harvey, H. R. & Johnston, J. R. 1995 Lipid composition and flux of sinking and size-fractionated particles in Chesapeake Bay. *Organic Geochemistry* **23,** 751–764.

Hedges, J. I. & Keil, R. G. 1999 Organic geochemical perspectives on estuarine processes: sorption reactions and consequences. *Marine Chemistry* **65,** 55–65.

Hedges, J. I., Keil, R. G. & Benner, R. 1997 What happens to terrestrial organic matter in the ocean? *Organic Geochemistry* **27,** 195–212.

Hedges, J. I. & Stern, J. H. 1979 Carbon and nitrogen determinations of carbonate-containing solids. *Limnology and Oceanography* **29,** 657–663.

Henrichs, S. M. & Reeburgh, W. S. 1987 Anaerobic mineralization of marine sediment organic matter: rates and the role of anaerobic processes in the oceanic carbon economy. *Geomicrobiology Journal* **5,** 191–237.

Holligan, P. M. & Reiners, W. A. 1992. Predicting the responses of the coastal zone to global change. *Advances in Ecological Research* **22,** 211–255.

Hood, R. R., Wang, H. V., Purcell, J. E., Houde, E. D. & Harding Jr., L. W. 1999 Modeling particles and pelagic organisms in Chesapeake Bay: convergent features control plankton distributions. *Journal of Geophysical Research* **104,** 1223–1243.

Johansson, E. & Sjodin, K. 1984 Minimizing the effects of closure on analytical data. *Analytical Chemistry* **56,** 1685–1688.

Kaiser, K. & Guggenberger, G. 2000 The role of DOM sorption to mineral surfaces in the preservation of organic matter in soils. *Organic Geochemistry* **31,** 711–725.

Kaneda, T. 1991 Iso- and anteiso-fatty acids in bacteria: biosynthesis, function, and taxonomic significance. *Microbiological Reviews* **55,** 288–302.

Karickoff, S. W., Brown, D. S. & Scott, T. A. 1979 Sorption of hydrophobic pollutants on natural sediments. *Water Research* **13,** 241–248.

Kemp, W. M. & Boynton, W. R. 1992 Benthic-pelagic interactions: nutrient and oxygen dynamics. In *Oxygen Dynamics in the Chesapeake Bay: A Synthesis of Recent Research*, (Smith, D. E., Leffler, M. & Mackiernan, G., eds). Maryland Sea Grant, College Park, MD. 234 pp.

Killops, S. D. & Killops, V. J. 1993 *An Introduction to Organic Geochemistry*. Longman Scientific and Technical, U.K. 265 pp.

Kuehl, S. A., Fuglseth, T. J. & Thunell, R. C. 1993 Sediment mixing and accumulation rates in the Sulu and South China Sea: implication for organic carbon preservation in deep-sea environments. *Marine Geology* **111,** 15–35.

Laureillard, J. & Saliot, A. 1993 Biomarkers in organic matter produced in estuaries: a case study of the Krka estuary (Adriatic Sea) using the sterol marker series. *Marine Chemsitry* **43,** 247–261.

Lee, C. 1992. Controls on organic carbon preservation: the use of stratified water bodies to compare intrinsic rates of decomposition in oxic and anoxic systems. *Geochimica et Cosmochimica Acta* **56,** 3323–3335.

Lee, C., Gagosian, R.G. & Farrington, J.W. 1977 Sterol diagenesis in Recent sediments from Buzzards Bay, Massachusetts. *Geochimica et Cosmchimica Acta* **41,** 985–992.

Lee, R. F., Hirota, J. & Barnett, A. M. 1971 Distribution and importance of wax esters in marine copepods and other zooplankton. *Deep-Sea Research* **18,** 1147–1165.

Malone, T. C. 1992. Effects of water column processes on dissolved oxygen, nutrients, phytoplankton and zooplankton. In *Oxygen Dynamics in the Chesapeake Bay: A Synthesis of Recent Research*, (Smith, D. E., Leffler, M. & Mackiernan, G., eds). Maryland Sea Grant, College Park, MD. 234 pp.

Malone, T. C., Crocker, L. H., Pike, S. E. & Wendler, B. W. 1988 Influences of river flow in the dynamics of phytoplankton production in a partially stratified estuary. *Marine Ecology Progress Series* **48,** 235–249.

Marshall, H. G. & Alden, R. W. 1993 Distribution of phytoplankton assemblages in the Chesapeake and Delaware Estuaries (USA), with emphasis on diatoms. *Hydrobiologia* **269/270,** 251–261.

Mayer, L. M. 1994*a* Relationship between mineral surfaces and organic carbon concnetration in soils and sediments. *Chemical Geology* **114,** 347–363.

Mayer, L. M. 1994*b* Surface area control of organic carbon accumulation in continental shelf sediments. *Geochimica et Cosmochimica Acta* **58,** 1271–1284.

Meglen, R. R. 1992 Examining large databases: a chemometric approach using principle component analysis. *Marine Chemistry* **39,** 217–237.

Meyers, P. A. 1994 Preservation of elemental and isotopic source identification of sedimentary organic matter. *Chemical Geology* **114,** 289–302.

Moreno, V. J., de Moreno, J. E. A. & Brenner, R. R. 1979 Biosynthesis of unsaturated fatty acids in the diatom *Phaeodactylum tricornutum*. *Lipids* **14,** 15–19.

Mudge, S. M. & Norris, C. E. 1997 Lipid biomarkers in the Conwy Estuary (North Wales, U.K.): a comparison between fatty alcohols and sterols. *Marine Chemistry* **57,** 61–84.

NAS/ODU, 1999 http://cobia.chesapeakebay.net/plankton. National Academy of Science/Old Dominion University.

Nichols, P. D., Jones, G. J., De Leeuw, J. W. & Johns, R. B. 1984 The fatty acid and sterol composition of two marine dinoflagellates. *Phytochemistry* **23,** 1043–1047.

Nichols, P. D., Klumpp, D. W. & Johns, R. B. 1982. Lipid components of the seagrasses *Posidonia australis* and *Heterozostera tasmanica* as indicators of carbon source. *Phytochemistry* **21,** 1613–1621.

Nixon, S. W. 1995 Coastal marine eutrophication: A definition, social causes, and future concerns. *Ophelia* **41,** 199–219.

Officer, C. B., Lynch, D. R., Setlock, G. H. & Helz, G. R. 1984 Recent sedimentation rates in Chesapeake Bay. In: *The Estuary as a Filter* (Kennedy, V. S., ed.). Academic Press, New York.

Ourisson, G., Albrecht, P. & Rohmer, M. 1979 The hopanoids: Paleochemistry and biochemistry of a group of natural products. *Pure and Applied Chemistry* **51,** 709–729.

Paoletti, C., Pushparaj, B., Florenzano, G., Capella, P. & Lercker, G. 1976 Unsaponifiable matter of green and blue-green algal lipids as a factor of biochemical differentiation of their biomass. *Lipids* **11,** 266–271.

Parkes, R. J. & Taylor, J. 1983 The relationship between fatty acid distributions and bacterial respiratory types in contemporary marine sediments. *Estuarine and Coastal Shelf Science* **16,** 173–189.

Parsons, T. R., Maika, Y. & Lalli, C. M. 1984 Determination of chlorophylls and total carotenoids: spectrophotometric method. In *A Manual of Chemical and Biological Methods for Seawater Analysis* (Majumdar, S. K., Hall, Jr., L. W. & Austin, H. M., eds). Pergamon Press, New York, NY, 573 pp.

Pennock, J. R. 1985 Chlorophyll distribution in the Delaware Estuary: regulation by light-limitation. *Estuarine and Coastal Shelf Science* **21,** 711–725.

Prahl, F. G., Ertel, J. R., Goni, M. A., Sparrow, M. A. & Eversmeyer, B. 1994 Terrestrial organic carbon contributions to sediments on the Washington margin. *Geochimica et Cosmochimica Acta* **58,** 3035–3048.

Rieley, G., Collier, R. J., Jones, D. M. & Eglinton, G. 1991 The biogeochemistry of Ellesmere Lake, U.K.-I: source correlation of leaf wax inputs to the sedimentary lipid record. *Organic Geochemistry* **17,** 901–912.

Robinson, N., Eglinton, G. & Brasswell, S. C. 1984 Dinoflagellate origin for sedimentary 4α-methyl steroids and 5α(H)-stanols. *Nature* **308,** 439–442.

Rohmer, M., Bouvier-Nave, P. & Ourisson, G. 1984 Distribution of hopanoid triterpenes in prokaryotes. *Journal of General Microbiology* **130,** 1137–1150.

Sellner, K. G. 1987 Phytoplankton in Chesapeake Bay: role in carbon, oxygen and nutrient dynamics. In*: Contaminant problems and management of living Chesapeake Bay resources* , (Majumdar, S. K., Hall, Jr., L. W. & Austin, H. M., eds). Pennsylvania Academy of Sciences, Philadelphia, pp. 134–157.

Sellner, K. G., Lacouture, R. V., Cibik, S. J., Brindley, A. & Brownlee, S. G. 1991 Importance of dinoflagellate-microflagellate bloom in the Patuxent River Estuary. *Estuarine, Coastal and Shelf Science* **32,** 27–42.

Sharp, J. H., Cifuentes, L. A., Coffin, R. B., Pennock, J. R. & Wong, K.-C. 1986 The influence of river variability on the circulation, chemistry, and microbiology of the Delaware Estuary. *Estuaries* **9,** 261–269.

Shaw, P. M. & Johns, R. B. 1985 Organic geochemical studies of a recent Inner Great Barrier Reef sediment—I. Assessment of input sources. *Organic Geochemistry* **8,** 147–156.

Shiah, F.-K. & Ducklow, H. W. 1994 Temperature regulation of heterotrophic bacterioplankton abundance, production, and specific growth rate in Chesapeake Bay. *Limnology and Oceanography* **39,** 1243–1258.

Smith, S. V. & Hollibaugh, J. T. 1993 Coastal metabolism and the oceanic organic carbon balance. *Reviews of Geophysics* **31,** 75–89.

Stribling, J. M. & Cornwell, J. C. 1997 Identification of important primary producers in a Chesapeake Bay tidal creek system using stable isotopes of carbon and sulfur. *Estuaries* **20,** 77–85.

Summons, R. E., Jahnke, L. L., Hope, J. M. & Logan, G. A. 1999 2-Methylhopanoids as biomarkers for cyanobacterial oxygenic photosynthesis. *Nature* **400,** 554–557.

Viso, A.-C. & Marty, J.-C. 1993 Fatty acids from 28 marine microalgae. *Phytochemistry* **34,** 1521–1533.

Volkman, J. K. 1986 A review of sterol markers for marine and terrigenous organic matter. *Organic Geochemistry* **9,** 83–99.

Volkman, J. K., Barret, S. M. & Blackburn, S. I. 1999 Eustigmatophyte microalgae are potential sources of C_{29} sterols, C_{22}-C_{28} *n*-alcohols and C_{28}-C_{32} *n*-alkyl diols in freshwater environments. *Organic Geochemistry* **30,** 307–318.

Volkman, J. K. & Hallegraeff, G. M. 1988 Lipids in marine diatoms of the genus *Thalassiosira*: predominance of 24-methylenecholesterol. *Phytochemistry* **27,** 1389–1394.

Volkman, J. K., Jeffrey, S. W., Nichols, P. D., Rogers, G. I. & Garland, C. D. 1989 Fatty acids and lipid composition of 10 species of microalgae used in mariculture. *Journal of Experimental Marine Biology and Ecology* **128,** 219–240.

Wakeham, S. G. 1989 Reduction of stenols to stanols in particulate matter at oxic-anoxic boundaries in sea water. *Nature* **342,** 787–790.

Wakeham, S. G. & Canuel, E. A. 1988 Organic geochemistry of particulate matter in the eastern tropical North Pacific Ocean: implications for particle dynamics. *Journal of Marine Research* **46,** 183–213.

Yunker, M. B., MacDonald, R. W., Veltkamp, D. J. & Cretney, W. J. 1995 Terrestrial and marine biomarkers in a seasonally ice-covered Arctic estuary—integration of multivariate and biomarker approaches. *Marine Chemistry* **49,** 1–50.

Zimmerman, A. R. 2000 Organic matter composition of sediments and the history of eutrophication and anoxia in Chesapeake Bay. Ph.D. Dissertation, College of William and Mary, School of Marine Science, Gloucester Point, VA.

Zimmerman, A. R. & Canuel, E. A. 2000 A geochemical record of eutrophication and anoxia in Chesapeake Bay sediments: anthropogenic influence on organic matter composition. *Marine Chemistry* **69,** 117–137.

Zitco, V. 1994 Principal component analysis in the evaluation of environmental data. *Marine Pollution Bulletin* **28,** 718–722.