Estuaries Vol. 22, No. 4, p. 980–994 December 1999

Composition of Particulate Organic Matter in the Southern Chesapeake Bay: Sources and Reactivity

ELIZABETH A. CANUEL[1]
ANDREW R. ZIMMERMAN
School of Marine Science/Virginia Institute of Marine Science
The College of William and Mary
P. O. Box 1346
Gloucester Point, Virginia 23062

ABSTRACT: The distribution of two classes of lipid biomarker compounds (fatty acids and sterols) was used in conjunction with several bulk parameters (total suspended solids, chlorophyll *a*, and particulate carbon and nitrogen concentrations) to examine spatial and temporal variability in the sources of particulate organic matter (POM) important to southern Chesapeake Bay. Based on these geochemical parameters, we found that suspended and sedimentary organic matter in the southern Chesapeake Bay is derived from autochthonous sources including a mixture of fresh and detrital phytoplankton, zooplankton, and bacteria. The dominant factor contributing to temporal variability during our study was phytoplankton productivity. Enrichments in particulate organic carbon, chlorophyll *a*, total fatty acids, total sterols, and a number of biomarkers specific to phytoplankton sources were found in particles collected from surface (1 m) and deep (1 m above the bottom) portions of the water column at several sites during the spring bloom in March 1996 and during a localized bloom in July 1995. Comparison of sites at the mouths of two tributaries (York and Rappahannock rivers) to southern Chesapeake Bay with two sites located in the bay mainstem indicates spatial variation in the composition of POM was not significant in this region of the bay. The energetic nature of this region of the Chesapeake Bay most likely contributes to the observed homogeneity. Comparison with biomarker studies conducted in other estuaries suggests the high levels of productivity characteristic of the Chesapeake Bay contribute to high background levels of POM.

Introduction

The composition of suspended and sedimentary particulate organic matter (POM) influences a number of key environmental processes such as the supply of food to benthic and pelagic organisms, water chemistry, sediment cohesiveness and stability, and the distribution of contaminants. The abundance and composition of POM can change substantially in response to variations in the biological and physical processes controlling its distribution. Given the dynamic nature of estuarine environments, gradients in the abundance and composition of POM may be pronounced. Physical processes influencing the transport and delivery of particles can vary over time scales from as short as minutes to hours (e.g., in response to tidal and wind resuspension or advection events) to time scales on the order of seasons to years. Key biological processes, such as primary production and respiration, fluctuate over a range of temporal scales in response to the availability of light and nutrients and the temperature regime. These agents alter the abundance, composition, and availability of organic matter to heterotrophic organisms and influence the incorporation of labile organic matter into pelagic and benthic food webs.

A useful approach for characterizing the origin, chemical nature, and reactivity of POM involves the application of biological markers or biomarkers. Biomarkers are "organic compounds whose chemical structure, or skeleton, is formed by living organisms and is sufficiently stable to be recognized" (Hunt 1979, p. 546) in materials such as suspended particles, sediments, and petroleum. Previous studies have used a number of biomarkers ranging in source specificity to evaluate the relative importance of different sources of organic matter associated with suspended and sedimentary particles in estuaries. Biomarkers include stable carbon and nitrogen isotopes (Haines 1977; Spiker and Schemel 1979; Peterson et al. 1985; Cifuentes et al. 1988; Lucotte et al. 1991), lignin oxidation products (Reeves and Preston 1989), and lipid biomarker compounds (Mayzaud et al. 1989; Lajat and Saliot 1990; Lajat et al. 1990; Canuel et al. 1995; Harvey and Johnston 1995; Canuel and Cloern 1996).

In the present study, we used two classes of lipid biomarker compounds (fatty acids and sterols), as well as bulk parameters (chlorophyll *a*, C:N) to examine the origins and to infer the reactivity of

[1] Corresponding author; tele: 804/684-7134; fax: 804/684-7250; e-mail: ecanuel@vims.edu.

POM associated with suspended particles and surficial sediments collected from four sites in southern Chesapeake Bay. Chesapeake Bay is the largest estuary in the continental United States, with a surface area of 7,740 km² and a drainage basin of 165,760 km² (Wright and Phillips 1988). Within its boundaries is an extremely complex and variable ecosystem that includes a variety of habitats (e.g., salt and freshwater marshes, seagrass beds, and riverine systems). Owing to the diversity of this system and the high level of productivity of the Chesapeake Bay ecosystem, one might expect substantial degrees of temporal and spatial variability in the delivery of labile and refractory POM. Studies conducted in diverse systems such as the Chesapeake Bay can provide insights regarding processes controlling the composition of POM in other estuaries. A further reason for characterizing sources of organic matter in the Chesapeake Bay is related to increases in the occurrence of hypoxia and anoxia, an increasingly common water quality problem in many estuaries. In recent years, nutrient inputs from sewage and agricultural sources have contributed to rates of phytoplankton production (and biomass) in excess of the bay's oxygen assimilation capacity (Malone 1992). Much of this organic matter is remineralized in the water column where decomposition of organic matter is dominated by heterotrophic bacteria. High concentrations of organic matter, coupled with physical features of the bay (e.g., bathymetry and water column stratification), have resulted in decreases in dissolved oxygen (DO) concentrations in bottom waters throughout much of Chesapeake Bay. Few studies have focused on identifying the specific sources of labile organic matter contributing to these high rates of organic matter respiration and associated depletions in DO (Jonas 1992). Of these studies, most have focussed on the mesohaline region of the bay and tributaries draining into that region (Sigleo and Macko 1985; Harvey and Johnston 1995; Sigleo 1996). Identifying the sources of POM in southern Chesapeake Bay is also important because this region may supply much of the organic matter to the mesohaline region where oxygen depletions are greatest due to the northward advection of higher salinity bottom waters (Jonas 1992).

Materials and Methods

Sample Collection

Samples were collected on May 8–9, July 24, and September 18–19, 1995, and March 14–15, 1996, from four sites in the lower Chesapeake Bay (Fig. 1). Physical features of the water column were recorded using a conductivity-temperature-depth (CTD) continuous profiling instrument with an

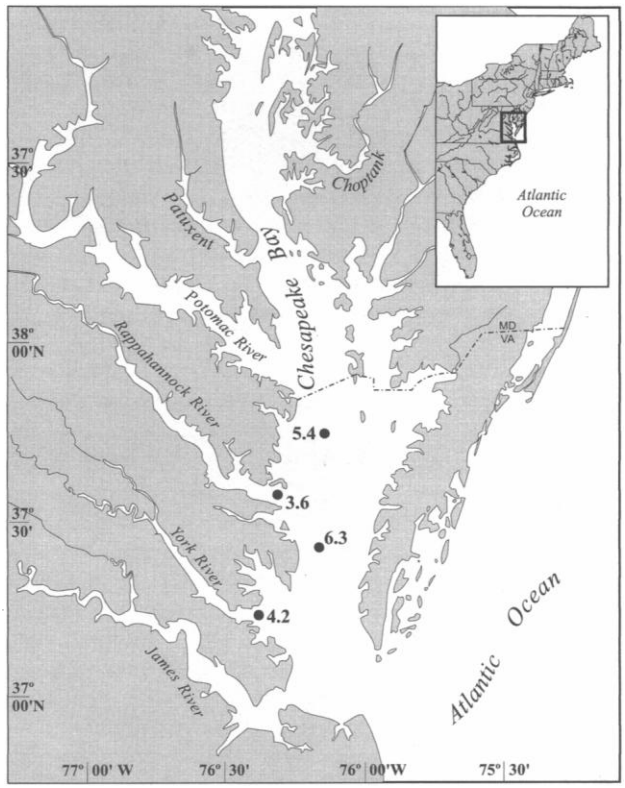

Fig. 1. Location of study sites in the southern Chesapeake Bay. Water depths at the mainstem stations (5.4 and 6.3) are 33 m and 12 m, respectively. The river mouth sites (3.6 and 4.2) have water depths of 10 m and 15 m, respectively.

oxygen electrode and in vivo fluorometer (Curling and Neilson 1994). On each sampling data, a single sample was collected from 1 m below the water surface and from 1 m above the sediment surface (hereafter, referred to as surface and deep, respectively) at each site. Water samples (4 l) were collected using a pump system attached to the continuous profiling instrument assembly. This water was subsampled and filtered for the measurement of the following bulk parameters: chlorophyll *a* (chl *a*), organic carbon and nitrogen, and suspended particle matter (SPM) concentrations. In addition, a peristaltic pump was used to obtain 40-l water samples, which were collected via 1-inch diam polyurethane (PUR) tubing attached to the CTD unit and pumped into stainless steel carboys onboard the research vessel. Two carboy volumes were collected and discarded to flush the tubing and rinse the carboys prior to sample collection. PUR and silicone tubing were used to avoid contamination (PUR tubing contains no plasticizers and very low levels of extractables). These samples were subsequently filtered and used for the organic geochemical analyses described below.

Surface sediments were collected using either a

Van Veen grab sampler or a box core (Ocean Instruments, San Diego, California). Water overlying the sampled sediments was removed by siphon and surface sediments (uppermost 0.25 cm) were collected using a solvent-rinsed spatula. Sediment samples were transferred to precombusted (450°C for 5 h) glass jars and placed in an ice chest aboard the ship. Upon return to the laboratory, all samples were stored in an ultra-cold freezer (at −80°C) until analyzed (within 6 mo of collection).

Bulk Parameters

SPM concentrations were determined by filtering 500-ml aliquots onto preweighed 47-mm diam glass-fiber filters (GF/AE). Particle masses were measured gravimetrically after samples were dried at 103°C. Chl *a* samples were collected onto 47-mm GF/AE filters, which were frozen immediately. The filters were ground and extracted in 90% acetone. Absorbances of the extracts were measured with a UV/VIS scanning spectrophotometer (Milton Roy Spectronic 1201) and chl *a* and phaeopigment concentrations calculated as described in Parsons et al. (1984). Particle and sediment samples were acidified to remove inorganic carbon (following the methods outlined in Hedges and Stern 1979) prior to elemental analysis using a Carlo Erba NA1500 elemental analyzer.

Organic Geochemical Analyses

As described above, large-volume water samples (40 l) were collected into stainless steel carboys. The carboys were sealed, pressurized with nitrogen (~8–10 psi), and the water passed through a stainless steel filter holder containing a precombusted (450°C) glass-fiber filter (142-mm diam; Gelman A/E). Total filtration time for each sample was generally about 4 h and carboys were shaken at regular intervals to keep particles suspended. Following filtration, glass-fiber filters were placed in precombusted jars and immersed in a 2:1 solution (v:v) of methylene chloride : methanol (May only) or chloroform : methanol (other samples; hereafter, we refer to chloroform only). Samples were stored as described above.

Before extraction, individual filters were torn into 1–2 cm pieces using solvent-rinsed forceps. Sample jars were placed in an ice bath and extracted for 10 min using an ultrasonic probe (5 min pulsed mode; 5 min continuous). After allowing samples to sit (overnight for the initial extraction and 1–2 h for subsequent extractions), the jars were centrifuged (1,500 rpm for 20 min) and the supernatant decanted into separatory funnels. The chloroform : methanol solution was renewed and the ultrasonic extraction was repeated two times. A solution of 20% NaCl in H_2O was then added to the combined extracts such that the final proportions were chloroform : methanol : water (2:2:1.8 by volume; Bligh and Dyer 1959). Samples were shaken and allowed to separate into two phases and the organic (lower) phase was collected. The filter or sediment was extracted a final time with hexane, which was then used to re-extract the aqueous phase. The combined organic phases were refrigerated overnight over anhydrous Na_2SO_4 to remove traces of water. The extract was concentrated using turbo-evaporation (Zymark Turbo Vap 500) and stored under N_2 in a small volume (~1 ml) of hexane.

A portion (10–50%) of the lipid extract was saponified using 1 N KOH (Canuel and Martens 1993 and references therein). The saponified sample was extracted into hexane under basic and acidic conditions, yielding neutral and acidic fractions respectively. The acids were methylated using 3% BF_3-CH_3OH and purified using a silica gel column. Neutral lipids were separated into constituent classes on a silica gel column using solvents of increasing polarity. Sterols were eluted with 15% and 20% ethyl acetate in hexane. This fraction was concentrated to 1 ml using turbo-evaporation, dried under N_2 and converted to trimethylsilyl (TMS) ethers using bis(trimethylsilyl)trifluoroacetamide (BSTFA). Fatty acids (as methyl esters) and sterols (as TMS ethers) were analyzed by gas chromatography (according to Canuel and Martens 1993). 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-cholestane for sterols). Identifications of components in selected samples were confirmed by gas chromatography-mass spectrometry (GC-MSD; Hewlett Packard 6890 Series Gas Chromatograph-Mass Selective Detector). The GC-MSD was operated at 70 eV and spectra were acquired over the 50–550 a.m.u. range. Fatty acids are designated as A:BωC, where A is the total number of carbon atoms, B is the number of double bonds, and C is the position of the first double bond from the aliphatic (ω) end of the molecule. Sterols are designated by carbon number and the "Δ" notation is used to indicate the position of double bonds.

Data Analysis

Data were imported into StatView (Abacus Concepts, Inc.) or MiniTab and analyzed statistically when possible given the limitations of the dataset (i.e., limited replication). Unless otherwise indicated, all confidence intervals are expressed at the 95% ($p = 0.05$) level. Correlation coefficients were

TABLE 1. Concentration and bulk composition of suspended particles.

Date	Site	Surface Particles					Deep Particles				
		SPM (mg l^{-1})	Chl *a* (μg l^{-1})	POC[a] (mg l^{-1})	PN (mg l^{-1})	C:N_a[b]	SPM (mg l^{-1})	Chl a (μg l^{-1})	POC[a] (mg l^{-1})	PN (mg l^{-1})	C:N_a
May 1995	3.6[c]	5.0	2.23	0.60	0.09	7.78	7.7	4.61	0.80	0.11	8.48
	4.2	10.2	3.77	0.56	0.09	7.26	18.0	3.66	0.70	0.11	7.42
	5.4	5.8	4.93	0.86	0.11	9.12	33.8	2.00	1.27	0.18	8.23
	6.3	5.5	1.45	0.49	0.08	7.15	13.8	2.93	0.56	0.10	6.53
Jul 1995	3.6	47.0	37.48	3.68	0.54	7.95	17.2	n.d[d]	0.69	0.14	5.75
	4.2	32.4	4.28	0.94	0.14	7.83	30.9	1.30	0.62	0.11	6.58
	5.4	18.1	0.72	0.88	0.14	7.33	28.6	n.d.	0.28	0.04	8.17
	6.3	17.2	2.77	0.70	0.13	6.28	33.8	n.d.	0.47	0.06	9.14
Sep 1995	3.6	9.3	5.64	0.93	0.17	6.38	11.3	0.66	0.56	0.11	5.94
	4.2	11.8	7.87	0.26	0.11	2.76	18.6	5.77	0.68	0.13	6.10
	5.4	8.6	4.55	0.45	0.11	4.77	43.0	5.34	1.04	0.16	7.58
	6.3	7.8	2.82	0.29	0.07	4.83	6.2	2.21	0.42	0.07	7.00
Mar 1996	3.6	7.5	7.43	0.67	0.11	7.11	10.1	25.90	2.10	0.30	8.17
	4.2	16.4	7.84	0.92	0.16	6.71	7.0	18.90	1.29	0.19	7.92
	5.4	6.2	4.06	0.42	0.09	5.44	18.4	19.22	1.59	0.24	7.73
	6.3	8.0	5.98	0.64	0.11	6.79	12.8	39.94	2.56	0.40	7.47

[a] May samples are particulate carbon (PC) instead of particulate organic carbon (POC).
[b] Elemental ratios calculated on a molar basis.
[c] Sites 3.6 and 4.2 are located at the mouths of the Rappahannock and York rivers, respectively; sites 5.4 and 6.3 are mainstem stations.
[d] Not detectable (n.d.).

obtained by analyzing for linear relationships between variables. Analysis of variance (ANOVA) was used to examine spatial variability by testing for significant differences between the riverine (sites 3.6 and 4.2; n = 8) and the mainstem sites (sites 5.4 and 6.3; n = 8). Spatial variability was also examined by grouping sites to represent the northern (sites 5.4 and 3.6; n = 8) and southern (sites 6.3 and 4.2; n = 8) regions. These analyses ignored time; temporal variability was examined separately by grouping the spring samplings (May 1995 and March 1996; n = 8) and comparing those data with non-spring samplings (July and September; n = 8).

Results

Bulk Parameters: Suspended Particles

Concentrations of suspended particulate matter (SPM) ranged from 5 mg l^{-1} to 47 mg l^{-1} and 6 mg l^{-1} to 43 mg l^{-1} in the surface and deep portions of the water column, respectively (Table 1). SPM concentrations were generally higher in surface waters collected from both of the river mouth sites (stations 3.6 and 4.2) than in the mainstem sites (stations 5.4 and 6.3), a similar trend was not observed for the deep waters. The range in chl *a* concentrations was similar for particles collected from the surface and deep regions of the water column (<1 μg l^{-1} to 40 μg l^{-1}; Table 1). In the surface waters, concentrations of chl *a* were correlated with SPM ($r = 0.76$, $p < 0.01$). No statistical relationship was found between these variables for particles collected from depth. In the surface waters, the highest chl *a* concentrations were measured at station 3.6 in July, and were associated with a localized red tide event. High chl *a* concentrations (19–40 μg l^{-1}) were also associated with suspended particles collected in deep water during March (Table 1). Using a conservative estimate (35) of the ratio of phytoplankton carbon to chl *a* (Wienke and Cloern 1987), we estimate that, on average, 20% of the POC is derived from phytoplankton, except during March (all sites) and July (station 3.6, surface) when the phytoplankton component of the carbon ranged from 30% to 55%.

In the surface waters, POC concentrations ranged from 0.26 mg l^{-1} to 3.68 mg l^{-1} at the river mouth sites and 0.29 mg l^{-1} to 0.88 mg l^{-1} at sites located in the mainstem (Table 1). In the deep waters, POC ranged from 0.56 mg l^{-1} to 2.10 mg l^{-1} and 0.28 mg l^{-1} to 2.56 mg l^{-1} at the river mouth and mainstem sites, respectively. Particulate nitrogen (PN) ranged from 0.07 mg l^{-1} to 0.54 mg l^{-1} in the surface waters and from 0.04 mg l^{-1} to 0.4 mg l^{-1} in the deep water. In general, a wider range of values was observed at the mainstem sites versus river mouth sites (Table 1). On a mass basis, POC made up 2–15% of the surface SPM. The POC content of the deep particles was somewhat more variable than for the surface particles (1–21%) with the highest organic contents found on particles collected during the spring phytoplankton bloom (in March). Elemental ratios expressed on a molar basis (C:N_a) were computed from the POC and PN concentration data. The range in C:

TABLE 2. Composition of surficial sediments.

Date	Site	TOC (mg g^{-1} sed)	TN (mg g^{-1} sed)	C:N_a
May 1995	3.6	25.29 (0.11)[a]	3.58 (0.08)	8.24
	4.2	17.64 (0.24)	2.76 (0.05)	7.47
	5.4	23.29 (0.66)	3.68 (0.09)	7.38
	6.3	5.67 (0.20)	0.86 (0.12)	7.69
Jul 1995	3.6	23.35 (0.27)	3.17 (0.002)	8.59
	4.2	22.25 (0.13)	3.53 (0.05)	7.35
	5.4	23.93 (0.27)	3.50 (0.01)	7.98
	6.3	5.92 (0.07)	1.60 (0.03)	4.32
Sep 1995	3.6	20.17 (0.20)	3.03 (0.05)	7.77
	4.2	18.45 (1.03)	3.02 (0.09)	7.13
	5.4	25.01 (0.12)	3.73 (0.07)	7.82
	6.3	4.26 (0.39)	0.61 (0.06)	8.15
Mar 1996	3.6	17.36 (0.36)	2.24 (0.07)	9.04
	4.2	35.57 (0.13)	4.95 (0.41)	8.40
	5.4	24.00 (0.64)	3.70 (0.42)	7.57
	6.3	10.18 (0.79)	1.08 (0.07)	11.00

[a] Average of duplicate analyses (± range).

N_a was similar for particles collected from both the surface and deep regions of the water column (4.8–9.1), with no obvious temporal or spatial trend (Table 1). An anomalously low value (2.76) was calculated for site 4.2 in September, possibly indicating higher contributions of protein-rich components to this sample. In the surface waters, POC concentrations were correlated with SPM ($r = 0.84$, $p < 0.01$) and chl *a* ($r = 0.93$, $p < 0.01$). POC was also correlated with chl *a* in the deep region of the water column ($r = 0.94$, $p < 0.01$), although no relationship with SPM was found for these samples.

Bulk Composition of Sediments

At the river mouth sites, TOC ranged from 17.4 mg g^{-1} to 35.6 mg g^{-1} dry sediment and TN ranged from 2.24 mg g^{-1} to 4.95 mg g^{-1} dry sediment (Table 2). Similar ranges were found at station 5.4 in the mainstem, although TOC and TN abundances were substantially lower at station 6.3 (4.3–10.2 mg g^{-1} and 0.6–1.6 mg g^{-1} dry sediment, respectively). The organic carbon content of the surface sediments was substantially lower than for the suspended particles (1.7–3.6% at the river mouth sites and 0.4–2.5% at the mainstem sites; see above). In general, sediment C:N_a ranged from 7 to 11 (Table 2). Station 6.3 was characterized by the greatest variation due to an anomalously low ratio (4.3) measured in July.

Fatty Acids

Total fatty acid (FA) concentrations (i.e., sum of individual compounds) associated with particles collected from the surface waters ranged from 9 μg l^{-1} to 590 μg l^{-1} at the riverine sites and 15 μg l^{-1} to 76 μg l^{-1} at the mainstem sites (Table 3). At the mainstem sites, FA concentrations were higher during both spring samplings (May 1995 and March 1996) relative to the summer and fall. This trend was not statistically significant. To account for changes in particle concentration and organic content and to allow for comparisons with the surface sediments, FA concentrations were normalized to organic carbon (OC). Carbon-normalized total FA concentrations ranged from 33 μg mg^{-1} to 160 μg mg^{-1} OC for water column particles at the riverine sites and 8 μg mg^{-1} to 162 μg mg^{-1} OC at the mainstem sites (Table 3). Thus, FAs represent 3–16% of the POC.

Suspended particles collected from 1 m above the bottom had a narrower range in FA concentrations than those collected from the surface waters. At the riverine sites, FA concentrations associated with the deep particles ranged from 21 μg l^{-1} to 186 μg l^{-1} (Table 3). As in surface waters, FA concentrations were lower at the mainstem sites, ranging from 8 μg l^{-1} to 146 μg l^{-1}. When normalized to the POC content of SPM, the FA concentrations associated with deep water particles ranged from 34 μg mg^{-1} to 144 μg mg^{-1} OC at the riverine sites and from 8 μg mg^{-1} to 92 μg mg^{-1} OC at the mainstem sites. These FA concentrations correspond to 3–14% of the POC at the riverine sites and 1–9% of the POC at the mainstem sites.

FA concentrations in the surface sediments ranged from 169 μg g^{-1} to 1,911 μg g^{-1} dry weight sediment and from 25 μg g^{-1} to 344 μg g^{-1} dry weight sediment for the riverine and mainstem sites, respectively (Table 3). FA concentrations normalized to the organic content of the sediments were substantially lower than those associated with the suspended particles; values ranged from 8 μg mg^{-1} to 54 μg mg^{-1} OC for sediments at the riverine sites and 6 μg mg^{-1} to 14 μg mg^{-1} OC for sediments collected from the mainstem sites. FA made up 0.8–5.4% and 0.6–1.4% of POC at the riverine and mainstem sites, respectively. No temporal trend was evident in the sedimentary FA concentrations except at station 4.2, which showed a threefold enrichment during the March 1996 sampling (Table 3). On an absolute basis, the lowest FA and POC concentrations were measured at site 6.3 in the Chesapeake Bay mainstem (Tables 2 and 3). However, when normalized to sediment organic carbon content, the FA concentrations at site 6.3 were comparable to those at the other study sites.

In addition to the above-described trends in FA concentrations, fatty acid composition also varied. Generally, monounsaturated and saturated acids were the most abundant fatty acids associated with both the water-column particles and surface sediments (Table 3). These fatty acids are common to many organisms and therefore provide little infor-

TABLE 3. Fatty acid concentrations in suspended particles and surface sediments.

Site	Sample	Date	Total Fatty Acids ($\mu g\ l^{-1}$ or $\mu g\ g^{-1}$ dry wt)[a]	Total Fatty Acids ($\mu g\ mg^{-1}$ OC)	Fatty Acid Groups[b]			
					%Saturated	%Monunsat	%Polyunsat	%Branched
3.6	Surface	May 1995	52.1	86.8	40.5	38.9	16.8	3.8
		Jul 1995	589.9	160.3	75.2	11.0	11.2	2.7
		Sep 1995	65.8	70.7	45.1	42.6	8.3	4.0
		Mar 1996	n/a	n/a	n/a	n/a	n/a	n/a
	Deep	May 1995	73.3	90.6	35.9	37.5	25.4	1.2
		Jul 1995	31.8	54.5	45.1	30.8	15.2	8.8
		Sep 1995	35.4	85.9	21.4	43.7	18.3	16.6
		Mar 1996	21.2	68.4	27.6	37.9	30.8	3.7
	Sediments	May 1995	376.1	14.9	31.5	45.0	14.1	9.4
		Jul 1995	382.0	16.4	40.2	38.4	4.9	16.5
		Sep 1995	168.5	8.2	40.2	39.0	4.9	15.9
		Mar 1996	215.8	12.5	26.4	43.2	19.2	11.2
4.2	Surface	May 1995	56.6	101.0	38.9	40.6	17.9	2.5
		Jul 1995	94.1	100.1	46.9	36.7	6.8	9.5
		Sep 1995	8.6	33.2	44.6	40.2	6.5	8.7
		Mar 1996	101.4	110.2	33.1	35.9	26.9	4.2
	Deep	May 1995	31.8	45.4	37.3	34.2	25.6	2.9
		Jul 1995	21.0	33.6	44.3	34.1	14.8	6.8
		Sep 1995	25.8	37.9	34.4	38.6	15.8	11.2
		Mar 1996	185.9	144.1	35.5	37.1	22.4	5.0
	Sediments	May 1995	224.3	12.7	34.4	35.8	14.4	15.4
		Jul 1995	418.8	18.8	38.7	35.9	4.9	20.5
		Sep 1995	243.1	13.2	41.0	38.3	3.8	16.9
		Mar 1996	1,911.4	53.7	41.1	22.5	21.7	14.8
5.4	Surface	May 1995	75.7	88.0	35.9	34.8	27.0	2.3
		Jul 1995	35.3	40.1	43.1	39.5	9.3	8.0
		Sep 1995	52.6	116.8	45.8	40.1	10.2	4.0
		Mar 1996	68.1	162.1	35.6	45.3	7.3	2.5
	Deep	May 1995	35.4	27.9	32.1	38.8	27.2	1.9
		Jul 1995	10.5	36.8	39.9	37.6	7.7	14.7
		Sep 1995	7.9	7.6	45.2	37.3	9.5	8.0
		Mar 1996	146.3	92.0	43.1	33.0	19.0	4.9
	Sediment	May 1995	285.9	12.3	37.2	38.4	14.0	10.4
		Jul 1995	282.2	11.8	36.2	36.2	5.4	22.1
		Sep 1995	263.4	10.5	39.3	37.8	3.7	19.2
		Mar 1996	344.3	14.3	31.7	43.4	5.0	19.9
6.3	Surface	May 1995	32.3	66.0	37.2	32.8	26.7	3.3
		Jul 1995	23.7	33.9	49.3	33.6	8.8	8.2
		Sep 1995	14.9	51.2	44.2	40.7	10.8	4.3
		Mar 1996	73.7	115.1	35.5	39.5	18.9	6.1
	Deep	May 1995	21.2	37.9	33.8	32.6	29.6	4.0
		Jul 1995	15.3	32.6	49.4	31.7	11.5	7.4
		Sep 1995	7.9	18.7	46.1	35.6	12.4	5.8
		Mar 1996	77.0	28.8	35.5	39.5	18.9	6.1
	Sediments	May 1995	68.8	12.1	32.9	38.4	14.5	14.2
		Jul 1995	37.5	6.3	37.6	37.9	5.4	19.1
		Sep 1995	24.8	5.8	39.1	37.4	8.6	14.8
		Mar 1996	70.6	6.9	55.9	28.9	6.3	9.0

[a] Concentrations for water-column particles are given in units $\mu g\ l^{-1}$ and for sediments on a $\mu g\ g^{-1}$ weight sediment basis.

[b] Fatty acid groupings were assigned based on the number of double bonds and whether the carbon chains were normal or contained methyl branches. Saturated fatty acids contain no double bonds; monounsaturated and polyunsaturated acids contain one and more than one double bond, respectively. Generally, fatty acid reactivity decreases with decreasing number of double bonds. Polyunsaturated fatty acids are commonly used as biomarkers for fresh plankton and branched fatty acids as biomarkers for bacteria.

mation regarding source. Branched acids, generally of bacterial origin, were also present but at lower concentrations (generally <20% of the total FAs). Generally, branched acids were more abundant in the surficial sediments (10–20%) than in association with suspended particles from the overlying water-column (generally <10%). Compared with the spring samplings (particularly March), when concentrations of polyunsaturated fatty acids of plankton origin were elevated (Table 3), branched fatty acids were generally more abundant during the warm months (July and September).

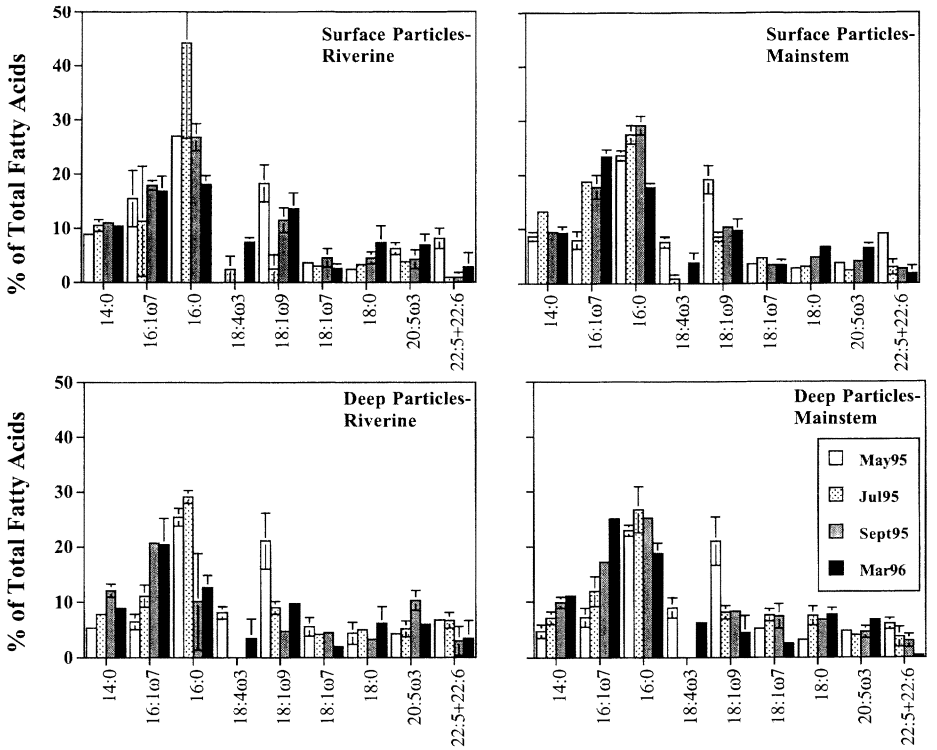

Fig. 2. Percent abundance of selected fatty acids expressed relative to the total fatty acid concentrations associated with surface and deep particles. Individual bars represent the average of two measurements (stations 3.6 and 4.2 for riverine sites and stations 5.4 and 6.3 for mainstem sites). Error bars represent the range. Compound designations refer to A:BωC where A is the number of carbon atoms, B is the number of double bonds, and C is the position of the first double bond from the aliphatic (ω) end of the molecule.

Samples were characterized by high concentrations of even-numbered, C_{14-18} saturated and monounsaturated acids and polyunsaturated C_{18-22} carboxylic acids (Figs. 2 and 3). Despite the complexity found in the fatty acid distributions (i.e., 30–40 individual fatty acids identified in most samples), a few compounds (e.g., 14:0, 16:0, 16:1ω7, 18:1, and 20:5ω3) generally made-up approximately 70% of the FA distribution (Figs. 2 and 3). Particulate polyunsaturated fatty acids were correlated with chl *a* concentrations both in the upper and lower portions of the water column ($r = 0.68$ and 0.73, respectively; $p < 0.01$).

Sterols

A complex assemblage of sterols was identified in this sample set. Particulate sterol concentrations at the riverine sites ranged from 3 μg l^{-1} to 89 μg l^{-1} in the surface waters and from 2 μg l^{-1} to 10 μg l^{-1} in the deep water (Table 4). At the main-

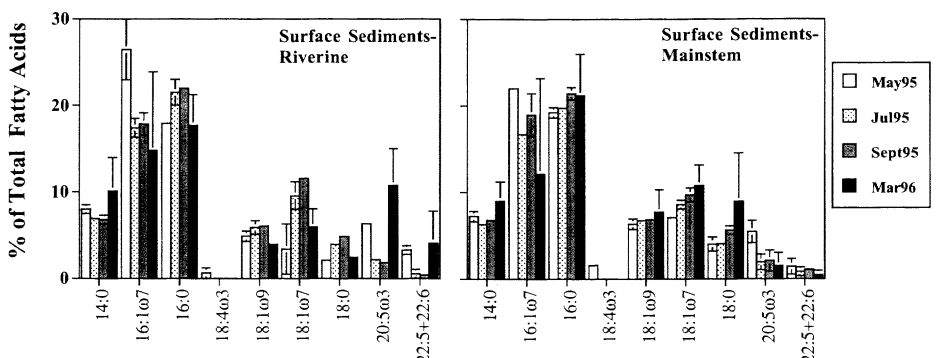

Fig. 3. Percent abundance of selected fatty acids expressed relative to the total fatty acid concentrations associated with the surficial sediments. Compound designations are as noted in the caption for Fig. 2.

TABLE 4. Sterol concentrations in suspended particles and surface sediments.

Site	Sample	Date	Total Sterols ($\mu g\ l^{-1}$ or $\mu g\ g^{-1}$ dry wt)[a]	Total Sterols ($\mu g\ mg^{-1}$ OC)	Sterol Groups[b]			
					$\%C_{27}$	$\%C_{28}$	$\%C_{29}$	%Others[c]
3.6	Surface	May 1995	2.7	4.5	20.0	51.1	20.0	8.9
		Jul 1995	89.0	24.2	5.8	58.3	31.0	5.0
		Sep 1995	2.7	2.9	34.2	41.3	14.0	10.3
		Mar 1996	12.6	18.8	14.8	54.7	16.1	14.4
	Deep	May 1995	3.1	3.8	15.3	41.7	32.1	10.9
		Jul 1995	2.3	10.5	44.7	24.4	18.3	12.6
		Sep 1995	1.6	5.5	43.7	27.1	14.7	14.5
		Mar 1996	1.5	2.9	17.8	56.7	15.5	10.0
	Sediments	May 1995	85.9	3.4	21.0	37.9	25.9	15.3
		Jul 1995	86.8	3.7	23.8	29.7	25.9	20.6
		Sep 1995	55.6	2.8	20.3	23.1	27.4	29.2
		Mar 1996	46.6	2.7	24.9	32.5	21.7	20.9
4.2	Surface	May 1995	2.9	5.1	23.8	54.4	19.4	2.4
		Jul 1995	9.6	10.2	58.7	25.3	13.8	2.2
		Sep 1995	3.5	13.5	32.6	44.0	13.2	10.2
		Mar 1996	6.4	7.0	24.4	45.4	15.8	14.3
	Deep	May 1995	2.3	3.3	24.1	41.2	18.8	16.0
		Jul 1995	3.7	5.9	45.4	25.9	19.7	9.0
		Sep 1995	4.3	6.3	34.0	39.5	14.7	11.8
		Mar 1996	9.6	7.4	23.1	47.8	14.1	15.0
	Sediments	May 1995	55.4	3.1	23.1	33.8	25.2	17.9
		Jul 1995	118.2	5.3	24.9	30.6	26.4	18.0
		Sep 1995	74.3	4.0	25.6	30.4	22.6	21.4
		Mar 1996	191.4	5.4	25.2	41.1	21.5	12.3
5.4	Surface	May 1995	2.9	3.3	18.7	49.6	24.3	7.3
		Jul 1995	8.2	9.3	35.9	30.7	18.3	15.1
		Sep 1995	3.1	6.8	40.2	38.1	14.6	7.2
		Mar 1996	3.3	7.9	21.2	52.7	16.5	9.6
	Deep	May 1995	1.6	1.3	23.6	46.6	18.8	11.0
		Jul 1995	1.9	6.5	44.2	28.2	19.8	7.7
		Sep 1995	2.6	2.5	36.4	29.5	17.4	16.7
		Mar 1996	9.3	5.8	19.4	51.9	16.4	12.3
	Sediment	May 1995	77.2	3.3	25.1	35.4	25.8	13.6
		Jul 1995	84.8	3.5	25.1	31.7	24.5	18.7
		Sep 1995	77.6	3.1	26.3	28.6	22.8	22.4
		Mar 1996	92.9	3.9	33.2	28.8	19.5	18.5
6.3	Surface	May 1995	1.8	3.6	20.2	42.1	25.3	12.3
		Jul 1995	1.9	2.7	36.7	29.5	20.7	13.1
		Sep 1995	1.0	3.4	43.9	37.4	12.1	6.6
		Mar 1996	5.2	8.2	17.6	47.4	21.1	13.9
	Deep	May 1995	1.5	2.7	26.6	38.4	21.4	13.6
		Jul 1995	3.6	7.7	62.6	18.8	12.8	5.8
		Sep 1995	0.9	2.2	59.4	22.1	11.8	6.6
		Mar 1996	17.4	6.8	20.9	46.4	17.9	14.8
	Sediments	May 1995	16.8	3.0	35.5	31.9	20.6	12.0
		Jul 1995	9.3	1.6	31.0	25.4	23.9	19.6
		Sep 1995	8.0	1.9	30.4	28.1	22.5	19.0
		Mar 1996	31.5	3.1	25.5	35.7	21.3	17.5

[a] Concentrations for water-column particles are given in $\mu g\ l^{-1}$ and for sediments on a $\mu g\ g^{-1}$ dry weight sediment basis.

[b] Sterols were grouped according to whether they contained 27, 28, or 29 carbon atoms. C_{27} sterols are comprised predominantly of cholest-5-en-3ß-ol (cholesterol), the dominant sterol in zooplankton. C_{28} sterols occur widely, although not exclusively, in phytoplankton while C_{29} sterols are generally derived from higher plants.

[c] Includes unidentified compounds, C_{30} sterols, and hopanols.

stem sites, particulate sterol concentrations ranged from 1 $\mu g\ l^{-1}$ to 8 $\mu g\ l^{-1}$ and 1 $\mu g\ l^{-1}$ to 17 $\mu g\ l^{-1}$ in the surface and deep waters, respectively. Sterol concentrations ($\mu g\ l^{-1}$) associated with water column particulate matter were about one fourth those found for the fatty acids. On a carbon-normalized basis, sterol concentrations ranged from 1 $\mu g\ mg^{-1}$ to 24 $\mu g\ mg^{-1}$ OC and representing <2.0% of the organic carbon content of the SPM and sediments (Table 4). Relative to organic carbon content, sterols were enriched in particles collected from the surface versus deep regions of the

water column. When normalized to POC, sterol concentrations were approximately an order of magnitude lower than FA concentrations.

Sterol concentrations in the surficial sediments ranged from 47 μg g^{-1} to 191 μg g^{-1} dry weight sediment and 8 μg g^{-1} to 93 μg g^{-1} dry weight sediment at the riverine and mainstem sites, respectively (Table 4). As was observed for the suspended particles, the highest concentrations for each site were generally found during the March 1996 sampling. Concentrations were also elevated during the July 1995 sampling at all of the sites except station 6.3. Sterol concentrations represented <0.5% of the sedimentary organic carbon.

The sterol distributions in both the water column and sediments included a mixture of C_{27}, C_{28}, and C_{29} compounds (Table 4). Although 20–30 individual sterols were identified in these samples, a few compounds generally dominated the sterol distributions. Seven compounds made up 50–70% of the sterols associated with surface particles and 65–88% of sterols associated with deep particles and sediments (Figs. 4 and 5). Cholest-5-en-3β-ol (27Δ5), 24-methylcholesta-5,22-dien-3β-ol (28Δ5,22), and 24-methylcholesta-5,24(28)-dien-3β-ol (28Δ5,24(28)) were generally the most abundant sterols associated with both the suspended particles and surficial sediments. Suspended particles were dominated by cholest-5-en-3β-l (27Δ5) during July and September while a more equal distribution of these three sterols was evident during the May and March samplings (Fig. 4).

Discussion

Sources of Organic Matter in the Lower Chesapeake

Fatty acid and sterol biomarkers indicate POM in the southern Chesapeake Bay is predominately derived from a mixture of autochthonous sources, including fresh and detrital phytoplankton, zooplankton, and bacteria. This is supported by high concentrations of compounds indicative of a mixed plankton community such as 14:0, 16:0, 16:1ω7, and polyunsaturated C_{18}, C_{20}, and C_{22} fatty acids. Although several of these compounds occur widely in organic matter of planktonic and bacterial origin (e.g., 14:0, 16:1ω7, and 16:0), they are not specific to these sources. The abundance of these more ubiquitous compounds, in addition to other compounds specific to phytoplankton, indicate that organic matter in the lower Chesapeake Bay is mostly of a planktonic/microbial source. For example, 20:5ω3, generally the dominant polyunsaturated fatty acid, is characteristic of diatoms (Volkman et al. 1989; Viso and Marty 1993). In addition, 18:4ω3 and 22:6ω3, commonly attributed to dinoflagellate sources of phytoplankton (Volkman et al. 1989; Nichols et al. 1984), were also present in most of our samples. In addition to diatom and dinoflagellate sources, cyanobacteria could be a likely source of organic matter as the fatty acids of these organisms are dominated by 16:0, 16:1ω7, and 18:1ω9 (Piorreck and Pohl 1984; Grimalt et al. 1992). Together, these compounds made up a substantial fraction of the fatty acids present in our samples (Figs. 2 and 3).

An autochthonous origin for POM in this region of the Chesapeake Bay is further supported by the sterol distributions. Throughout the study period, C_{27} and C_{28} sterols, typical of planktonic sources, dominated the suspended particle samples collected from our sites in the lower Chesapeake Bay (Table 4 and Figs. 4 and 5). Phytoplankton usually contains C_{28} sterols while zooplankton, of which crustaceans are the dominant class, often contain C_{27} sterols, particularly cholesterol (cholest-5-en-3β-ol; Killops and Killops 1993). In contrast, higher plants are generally dominated by C_{29} sterols (Huang and Meinschein 1979; Volkman 1986). Although these sterols are dominant in the organisms described above, they are not exclusive to those sources (i.e., some phytoplankton may contain low levels of C_{29} sterols, for example). Sterols known to be derived from diatoms such as 24-methylcholesta-5, 22-dien-3β-ol (28Δ5, 22), 24-methylcholesta-5, 24(28)-dien-3β-ol (28Δ5, 24(28)), and cholest-5-en-3β-ol (27Δ5) were most abundant in the lower CB during the periods when we sampled (Fig. 4). Dinosterol (4α, 23, 24-trimethylcholest-22-en-3β-ol), a sterol derived primarily from dinoflagellates (Volkman et al. 1989; Nichols et al. 1984), was also present in the samples but at lower levels than the diatom-derived biomarkers. Both the total C_{28} sterols and 24-methylcholesta-5, 22-dien-3β-ol concentrations associated with suspended particles (surface and deep) were highly correlated with chl *a* concentrations ($r = 0.95$, $p < 0.01$). Stable carbon isotopic signatures for seston and surficial sediments collected from this region as part of a subsequent study also support an autochthonous source for organic matter in this region of the Chesapeake Bay (−20 to −21‰; Canuel unpublished data).

Generally, concentrations of C_{29} sterols, common biomarkers for tracing vascular plants inputs (Volkman 1986), were low (<25% of total sterols) and exhibited little spatial or temporal variability (Table 4 and Figs. 4 and 5). Long-chain fatty acids (>*n*-C_{24}), also derived predominantly from vascular plant sources, were absent from the suspended particle samples and present at low concentrations in the surface sediments (Canuel unpublished data). Together this information suggests that allochthonous sources of organic matter are of con-

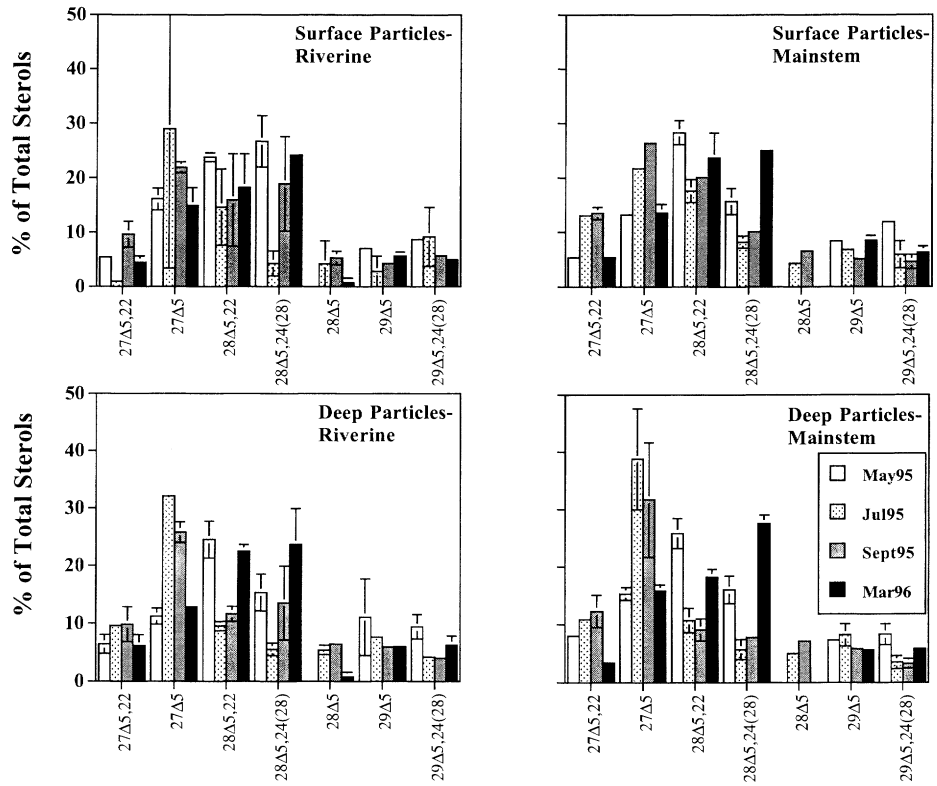

Fig. 4. Percent abundance of selected sterols expressed relative to the total sterol concentrations associated with surface and deep particles. Individual bars represent the average of two measurements (stations 3.6 and 4.2 for riverine sites and stations 5.4 and 6.3 for mainstem sites). Error bars represent the range. Compound designations are as follows: cholesta-5,22-dien-3β-ol (27Δ5,22), cholest-5-en-3β-ol (27Δ5), 24-methylcholesta-5,22-dien-3β-ol (28Δ5,22), 24-methylcholesta-5,24(28)-dien-3β-ol (28Δ5,24(28)), 24-methylcholest-5-en-3β-ol (28Δ5), 24-ethylcholest-5-en-3β-ol (29Δ5), and 24-ethylcholesta-5,24(28)-dien-3β-ol (29Δ5,24(28)). Sterols are designated as AΔX,Y where A refers to the total number of carbon atoms and ΔX,Y to the position of double bonds following the ring numbering conventions for steroids (Killops and Killops 1993).

siderably less importance than autochthonous sources to this region of the Chesapeake Bay. It also appears that fluctuations in the delivery of organic matter derived from terrigenous sources (i.e., vascular plants) to these sites were unimportant during the study period. The small contribution of organic matter derived from terrigenous sources is not surprising given the fact that rainfall and river flow, the primary mechanism for delivery of terrigenous organic matter, were below average during 1995. Flows were <1,800 $ft^3\ s^{-1}$ for the Pamunkey and Mattaponi rivers which drain into the

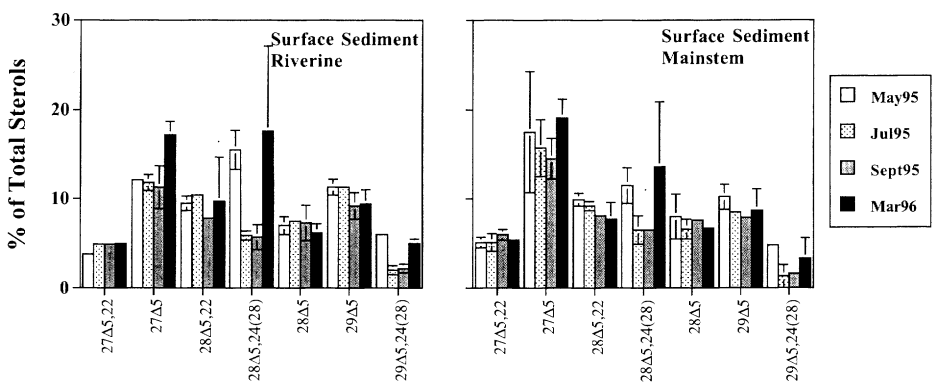

Fig. 5. Percent abundance of selected sterols expressed relative to the total sterol concentrations associated with surficial sediments. Compound identifications are the same as those provided in the caption to Fig. 4.

York and the Rappahannock rivers (United States Geological Survey Flow Data) during and for a few weeks prior to the periods when we sampled. Furthermore, even at the river mouth sites, gravitational circulation and tidal mixing may contribute to the dominance of organic matter from Bay sources except during large, episodic periods of high freshwater flow.

Branched fatty acids, generally indicative of bacterial sources of organic matter (Johns et al. 1977; Parkes and Taylor 1983), made up a small fraction (generally <10%) of the fatty acids associated with suspended particles (Table 3). Branched fatty acids of bacterial origin were most abundant in the July and September water column samplings while polyunsaturated fatty acids, derived exclusively from plankton sources, were generally more abundant during the spring samplings (May 1995 and March 1996). Branched fatty acids were also enriched in the surface sediments during July. An increase in the importance of bacterial activity during warm summer months (July and September) is also supported by depletions in the percent abundance of polyunsaturated fatty acids relative to organic carbon associated with water column particles versus sediments. We observed a general trend indicating a progressive depletion in the percent abundance of polyunsaturated fatty acids associated with water column particles relative to carbon-normalized concentrations found in the surface sediments. Polyunsaturated fatty acids made up 14.0 ± 2.5% and 18.3 ± 3.0% of the POC associated with the surface and deep particles, respectively, while these same compounds only made up 9.3 ± 2% of the sediment POC. Concomitantly, branched fatty acids of bacterial origin increase in their relative abundance (mean ± SD = 4.4 ± 0.7%, 6.5 ± 1.2%, and 15.6 ± 2.2% for surface particles, deep particles, and sediments, respectively). Fatty acid reactivity is thought to decrease with decreasing number of double bonds. Depletions in polyunsaturated fatty acids and enrichments in branched fatty acids in the surface sediments relative to particles in the overlying water column suggest organic matter associated with the surfacemost sediments is more degraded (i.e., less labile) than that associated with suspended particles. This is likely due to remineralization in the water column and/or at the water-sediment interface. The surface sediments may receive sources of organic matter different from those associated with suspended particles (e.g., soils and older, resuspended sediments). Increased abundances of branched fatty acids in the surface sediments may be due, in part, to differences in the in situ communities of bacteria relative to those associated with water column particulate matter.

Spatial and Temporal Variations in Particulate Organic Matter

We found little spatial variation in the composition of suspended particles at these four sites in the southern region of the Chesapeake Bay. With few exceptions, between-site concentrations of total fatty acids and total sterols varied by a factor of two to three. Complementary work indicates that this level of variation could easily be due to differences in tidal energy (Canuel unpublished data). The observed homogeneity in POM composition is probably due to the energetic, well-mixed nature of this region of the Chesapeake Bay. The southern region of the Chesapeake Bay and its adjoining tributaries are characterized by strong gravitational, tidal, and meteorological forcing (Wright et al. 1992). Tidally driven circulation dominates in this region of the bay with maximum tidal current speeds exceeding 100 cm s^{-1} observed near the surface (Wright et al. 1992 and references cited therein). In addition, recent attempts to model surface currents in the Chesapeake Bay have noted the existence of a large, convergent residual eddy in the lower bay that acts to concentrate particles and plankton (Hood et al. 1999). The physically energetic regime characteristic of the lower bay most likely contributes to the observed homogeneity in particle composition. CTD data collected during the May, September, and March samplings document that the water column was well mixed at each of the four sites (Chesapeake Bay Water Quality Monitoring Program unpublished data). The riverine sites were similarly well mixed during July; however, a pycnocline was observed at the mainstem stations, 6.3 and 5.4.

The suspended particle composition was similar at the four sites; however, we did find spatial variations in the surficial sediments, with sediments from station 6.3 generally depleted in organic content (i.e., TOC and biomarker concentrations) relative to the other three sites. Variability in sediment type and macrofaunal activity most likely contributes to these differences. The sediments at station 6.3 were coarser and had lower water content than those of the other sites. Previous work at or near this site documents that sediments from this region of the bay are heavily colonized and bioturbated, primarily by tube-dwelling organisms (Schaffner 1990).

The dominant factor contributing to temporal variability during our study appears to be phytoplankton production, with the highest concentrations of fatty acids and sterols associated with either localized or regional phytoplankton blooms. Although the sources of organic matter are predom-

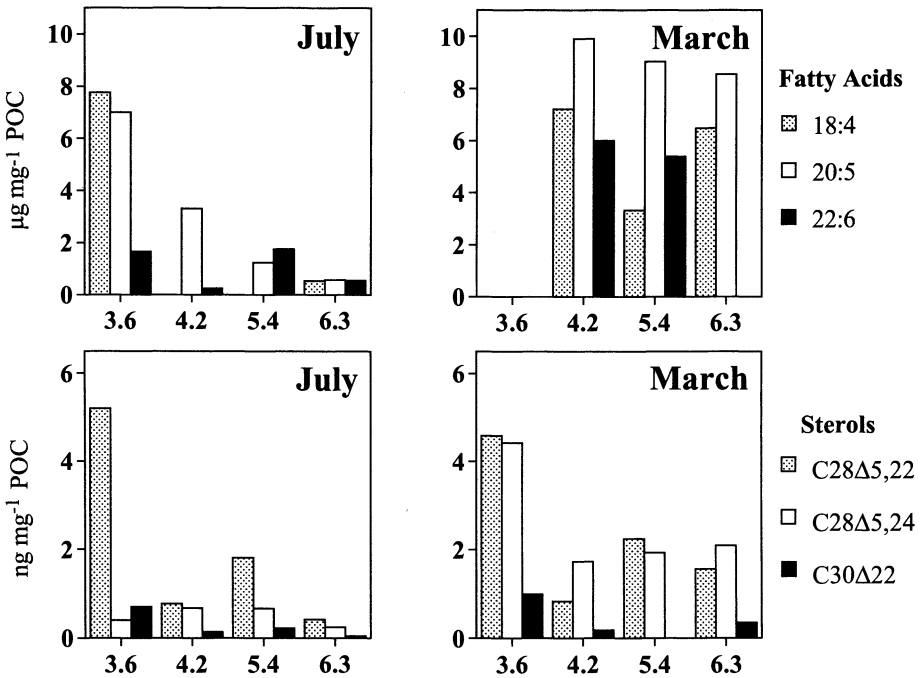

Fig. 6. Surface (1 m) particle concentrations of phytoplankton-derived fatty acids and sterols normalized to POC. Biomarker compounds attributable to dinoflagellate sources (C30Δ22 (dinosterol), $C_{18:4}$ and $C_{22:6}$) are proportionately more abundant during July, particularly at Stn 3.6. Diatom signatures ($C_{20:5}$, C28Δ5,22 and C28Δ5,24(28)) were evident at both time periods but dominated during the spring bloom sampled in March.

inantly autochthonous, biomarkers indicate there are temporal shifts in the phytoplankton assemblages. During July a localized red-tide event was observed visually and via remote sensing (http://noaa.chesapeakebay.net/) at station 3.6, and concentrations of chl *a*, POC, fatty acids, and sterols associated with surface particles increased by about an order of magnitude relative to other time periods (Tables 1, 3, and 4). In addition to changes in absolute concentrations (μg l^{-1}), relative to organic carbon, surface particles were enriched in fatty acids and sterols at station 3.6 at this time (Tables 3 and 4). Dinoflagellate blooms often reach red tide proportions in the lower bay during late spring and summer. Despite the presence of a diatom signature at all of the sites in July (e.g., 20:5ω3, 24-methylcholest-5,22-dien-3β-ol), dinoflagellate biomarkers were proportionately more abundant than during the spring bloom (Fig. 6). We measured the highest concentration (ng l^{-1}) of 4α, 23,24-trimethyl-5α-cholest-22-en-3β-ol (dinosterol), a biomarker often attributed to dinoflagellate sources (de Leeuw et al. 1983), at station 3.6 in July. In addition, polyunsaturated FAs were dominated by $C_{18:4}$ and $C_{22:6}$, characteristic of dinoflagellates. Although dinosterol may occur in some diatoms at trace concentrations (Volkman et al. 1993), the occurrence of this compound as well as fatty acid biomarkers support the increased importance of dinoflagellates in this bloom relative to the diatom-dominated spring bloom. This localized bloom event contributed to the higher variation (40–90%) in particulate fatty acid ($C_{16:1\omega7}$, $C_{16:0}$) and sterol biomarkers (27Δ5, 28Δ5,22, and 29Δ5,24(28)) for the two riverine sites (Figs. 4 and 5).

The spring phytoplankton bloom also contributed to temporal variability in our sample set. Ocean color data indicate high freshwater runoff and associated nutrient inputs resulted in a record-setting phytoplankton bloom during spring 1996 (surface chlorophyll data can be viewed at http://noaa.chesapeakebay.net/). This bloom persisted through the end of April in the lower bay and was dominated by pigment signatures characteristic of diatoms. Our sampling may have missed the period of highest chlorophyll concentrations; however, particulate fatty acid concentrations (normalized to POC, and in some cases on a volume-normalized basis) were generally highest in the water column of most of our sites during March 1996 (Fig. 3 and Table 3). Polyunsaturated fatty acids, derived exclusively from plankton, were also enriched at most of our sites during the March samplings (Table 3). These fatty acids are highly reactive and indicate an enrichment in labile organic matter during this time.

Comparisons With Previous Studies

Harvey and Johnston (1995) found concentrations of fatty acids that were similar to those found in our study in the mesohaline region of the Chesapeake Bay. Total fatty acids associated with bulk surface particles were 143 μg l^{-1} and 53 μg l^{-1} during spring and fall, respectively. Bottom water particle concentrations of fatty acids in the spring and fall were 315 μg l^{-1} and 32 μg l^{-1}, respectively. Compositionally, the fatty acid distributions were similar in both studies, with higher relative abundances of polyunsaturated fatty acids in spring versus fall. Polyunsaturated fatty acids made up a larger fraction of the FA (~50%) at the mesohaline site than we found in the lower bay (~20%). As described above, polyunsaturated fatty acids are derived from fresh phytoplankton and represent labile organic matter. Higher levels of polyunsaturated fatty acids in the mid bay relative to those found in southern Chesapeake Bay support the idea that organic matter may be less degraded in the mesohaline region. The high-energy regime characteristic of the lower Chesapeake Bay probably results in increased rates of sediment resuspension, which can lead to efficient recycling of organic matter. Higher recycling efficiencies have been linked to reoxidation of organic matter, fluctuating redox conditions, release of metabolites, and co-metabolism of refractory organic matter as new, labile constituents are introduced (Aller 1998). The increased availability of labile organic matter in the mesohaline region is also supported by observations that community respiration is highest in this region of the Chesapeake Bay (Smith and Kemp 1995). Alternatively, interannual variations in the timing and intensity of the spring bloom could account for observed differences in the abundance of labile organic matter in the mesohaline (Harvey and Johnston 1995) versus the lower region (this study).

During spring the sterol concentrations associated with bulk particles collected at the mesohaline site were 8 μg l^{-1} and 19 μg l^{-1} for surface and bottom particles, respectively (Harvey and Johnston 1995). Surface and bottom particle concentrations of sterols decreased to 3 μg l^{-1}, during their fall sampling. In our study, sterol distributions were dominated by compounds derived from phytoplankton (e.g., diatoms and dinoflagellates) in the spring. In the lower bay, the relative abundance of cholest-5-en-3β-ol was higher in particles collected in the fall than in the spring. The lipid composition of suspended material in southern Chesapeake Bay appears to be less variable seasonally than that of the mesohaline region, perhaps due to the greater importance of physical mixing in the southern region.

Concentrations of fatty acids and sterols were substantially higher in the Chesapeake Bay than in San Francisco Bay. Fatty acid concentrations associated with particles collected from 2 m below the surface ranged from 3 μg l^{-1} to 75 μg l^{-1} in southern San Francisco Bay and from 3 μg l^{-1} to 9 μg l^{-1} at the mouth of the Sacramento River (Canuel and Cloern 1996). Sterol concentrations in the southern and riverine regions of San Francisco Bay ranged from 0.6 μg l^{-1} to 5.5 μg l^{-1} and from 0.7 μg l^{-1} to 4.2 μg l^{-1}, respectively. Even at the height of the phytoplankton bloom in the southern region of San Francisco Bay, lipid concentrations were lower than during baseline (i.e., non-bloom) conditions in the Chesapeake, indicating the substantially higher productivity and lability of organic matter in the Chesapeake Bay.

Particulate sterol concentrations in the Chesapeake Bay were generally higher than values reported for other estuarine systems (summarized in Laureillard and Saliot 1993), although they were comparable to those measured in the Ariake Sea (Japan) where sterol concentrations ranged from 6 μg l^{-1} to 85 μg l^{-1} (Kanazawa and Teshima 1978). Sterol concentrations in the Chesapeake exceeded values reported for the Rhône delta, Mediterranean Sea (17–60 ng l^{-1} in July 1988 and 380–3,100 ng l^{-1} in December 1981 and January 1989; Scribe et al. 1989; Scribe et al. 1991), the Bedford Basin (300–5,000 ng l^{-1}; Pocklington et al. 1987), and the Krka estuary (441–724 ng l^{-1}; Laureillard and Saliot 1993). Comparable data for fatty acids distributions in estuarine systems were unavailable. Given the comparison with the San Francisco Bay data and the fact that fatty acid concentrations are several fold higher than sterols, it is reasonable to expect that fatty acid concentrations in Chesapeake Bay are high relative to other estuaries. These cross-system comparisons suggest that high, constant background levels of particles with high organic contents are representative of the southern Chesapeake Bay, and that concentrations of biomarker compounds from autochthonous sources are higher than those found in other estuaries.

Conclusions

Our analysis of lipid biomarker compounds associated with suspended particles and surficial sediments collected from the southern region of the Chesapeake Bay has provided useful insights regarding the sources and composition of POM in this economically and ecologically important estuary. Suspended and sedimentary organic matter in the southern Chesapeake Bay was largely derived from autochthonous sources and was composed of

a mixture of fresh and detrital phytoplankton, zooplankton, and bacteria. The strongest factor contributing to temporal variability during our study appeared to be phytoplankton production; summer blooms were dominated by dinoflagellate signatures whereas spring blooms were enriched in diatom biomarker compounds. Fatty acid and sterol biomarkers indicated an increase in the abundance of heterotrophic organisms (bacteria and zooplankton) during summer months. The relative abundance of bacterial biomarkers (branched FAs) was higher in the surface sediments than in the SPM, indicating that a larger fraction of the sedimentary POM was derived from bacterial biomass. Despite the relatively shallow water column of the estuary, sedimentary organic matter was more degraded relative to POM collected from the overlying water column. Terrigenous sources were found to be unimportant during this study most likely due to low river flow resulting from the dry conditions characteristic of 1995. The spatial homogeneity in POM composition we found in the southern bay was likely related to the physical energy regime and particle convergence. The dynamic nature of the lower bay may also have contributed to more efficient recycling of organic matter relative to that observed in previous studies conducted in the lower energy mesohaline region. Despite differences in particle composition within the bay, comparisons with other estuaries suggest high levels of productivity in the Chesapeake Bay contribute to higher background levels of organic-rich particles relative to other estuaries.

Acknowledgments

We would like to thank participants in the VIMS component of the Chesapeake Bay Water Quality Monitoring Program (WQMP) for allowing us to coordinate our field activities with their study and for providing unpublished data. Steve Snyder, Sam Wilson, Krisa Murray, and Grace Battisto provided able assistance in the field. Shannon Burcham assisted in the laboratory and with data analysis. Durand Ward and Charles Machen were very helpful in their capacity as captains of the R/V *Bay Eagle* and R/V *Langley*, respectively. This study was primarily supported by the Virginia Water Resources Research Center. Additional support was provided through grants from the National Science Foundation (OCE-9521170) and the Harbor Processes Program, Office of Naval Research (N00014–96–0062). This is contribution 2225 of the Virginia Institute of Marine Science.

Literature Cited

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

Bligh, E. G. and W. M. Dyer. 1959. A rapid method of lipid extraction and purification. *Canadian Journal of Biochemistry and Physiology* 35:911–917.

Canuel, E. A. and J. E. Cloern. 1996. Regional differences in the origins of organic matter in the San Francisco Bay Ecosystem: Evidence from lipid biomarkers, p. 305–324. *In* J. T. Hollibaugh (ed.), San Francisco Bay: The Ecosystem. American Association for the Advancement of Science, San Francisco.

Canuel, E. A., J. E. Cloern, D. B. Ringelberg, J. B. Guckert, and G. H. Rau. 1995. Molecular and isotopic tracers use 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. and C. S. Martens. 1993. Seasonal variations in the sources and alteration of organic matter associated with recently-deposited sediments. *Organic Geochemistry* 20:563–577.

Cifuentes, L. A., J. H. Sharp, and M. L. Fogel. 1988. Stable carbon and nitrogen isotope biogeochemistry of the Delaware estuary. *Limnology and Oceanography* 33:1102–1115.

Curling, K. and B. Neilson. 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.

Grimalt, J. O., R. de Wit, P. Teixidor, and J. Albaiges. 1992. Lipid biogeochemistry of *Phormidium* and *Microcoleus* mats. *Organic Geochemistry* 19:509–530.

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

Haines, E. B. 1977. The origins of detritus in Georgia salt marsh estuaries. *Oikos* 29:254–260.

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

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

Huang, W.-Y. and W. G. Meinschein. 1979. Sterols as ecological indicators. *Geochimica et Cosmochimica Acta* 43:739–745.

Hunt, J. 1979. Petroleum Geochemistry and Geology. W. H. Freeman and Company, San Francisco, California.

Johns, R. B., G. J. Perry, and K. S. Jackson. 1977. Contribution of bacterial lipids to recent marine sediments. *Estuarine, Coastal and Marine Science* 5:521–529.

Jonas, R. B. 1992. Microbial processes, organic matter and oxygen demand in the water column, p. 113–148. *In* D. E. Smith, M. Leffler, and G. Mackiernan (eds.), Oxygen Dynamics in the Chesapeake Bay: A Synthesis of Recent Research. Maryland Sea Grant, College Park, Maryland.

Kanazawa, A. and S. Teshima. 1978. The occurrence of coprostanol, an indicator of faecal pollution, in seawater and sediments. *Oceanologica Acta* 1:39–44.

Killops, S. D. and V. J. Killops. 1993. An Introduction to Organic Geochemistry. Longman Scientific and Technical, Essex, United Kingdom.

Lajat, M. and A. Saliot. 1990. Sterol composition of suspended matter from the Changjiang Estuary and adjacent East China Sea, p. 642–666. *In* G. H. Yu, J. M. Martin, and J. Y. Zhou (eds.), Biogeochemical Study of the Changjiang Estuary. China Ocean Press, Beijing.

Lajat, M., V. Denant, and A. Saliot. 1990. Selected organic matter source indicators in the Changjiang estuary and adjacent East China Sea: Sterol and fatty acid distributions in surface sediments, p. 688–704. *In* G. H. Yu, J. M. Martin, and J. Y. Zhou (eds.), Biogeochemical Study of the Changjiang Estuary. China Ocean Press, Beijing.

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

de Leeuw, J. W., F. W. Van Der Meer, W. I. C. Rijpstra, and P. A. Schenk. 1983. Free, esterified and residual bound sterols

in Black Sea Unit I sediments. *Geochimica et Cosmochimica Acta* 47:455–465.

LUCOTTE, M., C. HILLAIRE-MARCEL, AND P. LOUCHOUARN. 1991. First-order organic carbon budget in the St. Lawrence Lower Estuary from ^{13}C data. *Estuarine, Coastal and Shelf Science* 32: 297–312.

MALONE, T. C. 1992. Effects of water column processes on dissolved oxygen, nutrients, phytoplankton and zooplankton, p. 61–112. *In* D. E. Smith, M. Leffler, and G. Mackiernan (eds.), Oxygen Dynamics in the Chesapeake Bay: A Synthesis of Recent Research. Maryland Sea Grant, College Park, Maryland.

MAYZAUD, P., J. P. CHANUT, AND R. G. ACKMAN. 1989. Seasonal changes in the biochemical composition of marine particulate matter with special reference to fatty acids and sterols. *Marine Ecology Progress Series* 56:189–204.

NICHOLS, P. D., G. J. JONES, J. W. DE LEEUW, AND R. B. JOHNS. 1984. The fatty acid and sterol composition of two marine dinoflagellates. *Phytochemistry* 23:1043–1047.

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

PARSONS, T. R., Y. MAIKA, AND C. M. LALLI. 1984. Determination of chlorophylls and total carotenoids: Spectrophotometric method, p. 101–106. *In* T. R. Parsons, Y. Maika, and C. M. Lalli (eds.), A Manual of Chemical and Biological Methods for Seawater Analysis. Pergamon Press, New York.

PETERSON, B. J., R. W. HOWARTH, AND R. H. GARRITT. 1985. Multiple stable isotopes used to trace the flow of organic matter in estuarine food webs. *Science* 227:1361–1363.

PIORRECK, M. AND P. POHL. 1984. Formation of biomass, total protein, chlorophylls, lipids and fatty acids in green and blue-green algae during one growth phase. *Phytochemistry* 23:217–223.

POCKLINGTON, R. J., J. D. LEONARD, AND N. F. CREWE. 1987. Le coprostanol comme indicateur de la contamination fecale dans l'eau de mer et les sediments marins. *Oceanologica Acta* 10:83–89.

REEVES, A. D. AND M. R. PRESTON. 1989. The composition of lignin in estuarine suspended particulates and the distribution of particulate lignin in estuaries as determined by capillary gas chromatography of cupric oxide oxidation products. *Estuarine, Coastal and Shelf Science* 29:583–599.

SCHAFFNER, L. C. 1990. Small-scale organism distributions and patterns of species diversity: Evidence for positive interactions in an estuarine benthic community. *Marine Ecology Progress Series* 61:107–117.

SCRIBE, P., C. PEPE, C. FUCHE, C. BARREAU, R. SEMPERE, I. BOULOUBASSI, AND A. SALIOT. 1989. Application of the biogeochemical marker approach for determining the inputs and fate of biogenic and anthropogenic organic matter in the Rhone delta: Non-aromatic hydrocarbons and sterols associated to particles. *Water Pollution Research Reports* 13:173–178.

SCRIBE, P., C. BARREAU, C. PEPE, C. FUCHE, J. DAGAUT, AND A. SALIOT. 1991. Fluvial inputs of organic matter from the Rhône river to the northwestern basin of the Mediterranean Sea: Sterol composition of organic matter. *Water Pollution Research Reports* 20:259–267.

SIGLEO, A. C. 1996. Biochemical components in suspended particles and colloids: Carbohydrates in the Potomac and Patuxent estuaries. *Organic Geochemistry* 24:83–93.

SIGLEO, A. C. AND S. A. MACKO. 1985. Stable isotope and amino acid composition of estuarine dissolved colloidal material, p. 29–46. *In* A. C. Sigleo and A. Hattori (eds.), Marine and Estuarine Geochemistry. Lewis Publishers, Inc., Chelsea, Michigan.

SMITH, E. M. AND W. M. KEMP. 1995. Seasonal and regional variations in plankton community production and respiration for Chesapeake Bay. *Marine Ecology Progress Series* 116:217–231.

SPIKER, E. C. AND L. E. SCHEMEL. 1979. Distribution and stable isotope composition of carbon in San Francisco Bay, p. 195–212. *In* T. J. Conomos (ed.), San Francisco Bay: The Urbanized Estuary. American Association for the Advancement of Science, San Francisco, California.

VISO, A.-C. AND J.-C. MARTY. 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., S. W. JEFFREY, P. D. NICHOLS, G. I. ROGERS, AND C. D. GARLAND. 1989. Fatty acid and lipid composition of 10 species of microalgae used in mariculture. *Journal of Experimental Marine Biology and Ecology* 128:219–240.

VOLKMAN, J. K., S. M. BARRETT, G. A. DUNSTAN, AND S. W. JEFFREY. 1993. Geochemical significance of the occurrence of dinosterol and other 4-methyl sterols in a marine diatom. *Organic Geochemistry* 20:7–15.

WIENKE, S. M. AND J. E. CLOERN. 1987. The phytoplankton component of seston in San Francisco Bay. *Netherlands Journal of Sea Research* 21:25–33.

WRIGHT, D. A. AND D. J. H. PHILLIPS. 1988. Chesapeake and San Francisco Bays. A study in contrasts and parallels. *Marine Pollution Bulletin* 19:405–413.

WRIGHT, L. D., J. D. BOON, J. P. XU, AND S. C. KIM. 1992. The bottom boundary layer of the bay stem plains environment of lower Chesapeake Bay. *Estuarine, Coastal and Shelf Science* 35: 17–36.

SOURCE OF UNPUBLISHED MATERIALS

Chesapeake Bay Water Quality Monitoring Program data available at http://www.chesapeakebay.net/data

Received for consideration, July 28, 1998
Accepted for publication, April 30, 1999