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Diagenesis of planktonic fatty acids and sterols in Long Island Sound sediments: Influences of a phytoplankton bloom and bottom water oxygen content

by Ming-Yi Sun[1] and Stuart G. Wakeham[2]

ABSTRACT

Diagenesis of organic matter in coastal sediments from Long Island Sound (LIS) was investigated by measuring fatty acids and sterols in (1) a time-series of surface sediment samples over a spring phytoplankton bloom; and (2) sediment cores collected during and after a bloom at two sites with distinctively different bottom-water oxygen contents. Time-dependent distributions of sedimentary fatty acids and sterols in LIS were strongly affected by pulsed inputs from the overlying water column, variations in benthic community, and redox-related degradation processes. The phytoplankton bloom delivered an intense pulse of unsaturated fatty acids (e.g., 16:1(ω7) and 20:5) to the surface sediments. Continuous increases of cholesterol and diunsaturated sterols after the bloom were related to zooplankton grazing processes and increase in benthic faunal abundance. High inventories of planktonic fatty acids and sterols in the upper 5 cm sediments were observed at the low oxygen site during summer, probably caused by a combination of higher input, reduced degradation rates and lower macrofaunal activity under anoxic conditions compared to oxic conditions.

1. Introduction

Degradation of organic matter is an important process affecting the geochemistry of carbon, nutrients, and trace metals in coastal sediments. A major source of organic matter to coastal sediments is from planktonic detritus. Seasonal variability in primary production, zooplankton grazing, and sedimentation strongly influence the delivery of organic matter from surface waters to bottom sediments; organic matter delivery rates in turn affect benthic activity. Environmental factors such as oxygen content of bottom water and sediments also affect the structure of the benthic community and rates of biogeochemical cycling of organic matter. High productivity coupled with high sedimentation rate enhance organic matter preservation in sediments (Calvert *et al.,* 1991; Henrichs and Reeburgh, 1987). However, the effect of oxygen content on the degradation/preservation of organic matter in sediments is less certain (Emerson and Hedges, 1988; Pedersen and Calvert, 1990; Lee, 1992; Cowie *et al.,* 1995; Smith *et al.,* 1996).

1. Department of Marine Sciences, University of Georgia, Athens, Georgia, 30602, U.S.A. ***email: mysun@arches.uga.edu***

2. Skidaway Institute of Oceanography, Savannah, Georgia, 31411, U.S.A.

One key difference between oxic and anoxic environments is the abundance of benthic organisms. Benthic animals affect decomposition of organic matter in sediments in numerous ways, including particle fragmentation, direct grazing, and bioturbation. Particle reworking and irrigation by benthic fauna, leading to fluctuating or oscillating redox conditions in surface sediments, is an important factor affecting the remineralization of organic matter (Aller, 1994a). However, the role of benthic organisms in regulating degradation of organic matter in sediments under variable redox conditions is poorly understood (Aller, 1982; Kristensen and Blackburn, 1987; Lee, 1992).

The occurrence of anoxia in bottom waters and sediments has been attributed to a high flux of labile organic matter to the benthic boundary layer. The combination of high productivity and short water column in coastal areas results in the delivery of large amounts of labile organic matter to sediments. Subsequently, organic matter decomposition rapidly consumes dissolved oxygen, leading to anoxia in bottom waters and sediments. Thus, the roles of organic matter flux vs. bottom water and sediment redox conditions are important in understanding why it is that continental margin sediments, although comprising only ~10% of the seafloor, are the site of burial of ~90% of the organic matter buried in sediments of the world ocean (Berner, 1982). However, while most studies have focused on the long-term preservation, the effects of temporal variations in organic matter flux and bottom water and sediment oxygen content on early stages of degradation of organic matter have been investigated in only a few studies (Klump and Martens, 1981; Canuel and Martens, 1996).

This study was designed to examine the early diagenesis of planktonic fatty acids and sterols in a coastal sediment subject to varying surface water primary production and bottom water and sediment oxygen content. Distributions of fatty acids and sterols were tracked in surface sediments at one site (central LIS) over a 200-d period during which a spring bloom occurred (LIS-PULSE experiment). These results provide information about the effects of a pulsed delivery of planktonic organic matter to LIS sediments. Fatty acids and sterols were also measured as a function of depth in sediment cores from two sites with different redox environments and during two seasons characterized by different organic matter delivery rates. Monitoring changes in profiles of these lipid compounds and modeling for degradation rate constants allow us to examine the effects of redox conditions on diagenesis of organic matter in the sediments.

2. Experimental

a. Study locations and sampling

Time-series sampling (2–3 week intervals) started in December 1992 and lasted to July 1993 at central LIS station P (PULSE study, Gerino *et al.,* 1998). Eleven surface 0–0.5 cm sediment samples were collected and analyzed for lipids. The spring bloom was tracked by collecting surface water samples for Chl-*a* analysis every 3–4 days from the Port-Jefferson-Bridgeport Ferry as it transited central Sound during the study period.

Sediment cores for determination of depth distributions of lipids were collected in

central (station P) and western (station A) LIS during August, 1988, and February, 1989. All sediment samples were collected using a Soutar-style box corer and subcores (~10 cm length) were sliced into 0.5–1 cm intervals between 0–5 cm and into 2–3 cm intervals between 5–10 cm depth. These two sites represent different depositional environments with distinct redox conditions. Dissolved oxygen content (Mackin *et al.,* 1991) in bottom waters and surface sediments and solid Mn (Aller, 1994b) profiles (Fig. 1) varied differently with seasons at these sites. Central LIS water (station P) is oxygenated throughout the year while hypoxia (defined as $O_2 < 3$ mg/L) occurs in bottom waters at station A and the underlying sediment becomes anoxic during summer (Beristain and Arnold, 1991; Mackin *et al.,* 1991; Parker and O'Reilly, 1991). Solid reactive Mn, as a secondary oxidant and redox intermediate between O_2 and organic carbon, exists in surface sediments at these two sites when oxygen content is high but drops to almost zero in surface sediments when oxygen is absent at station A during summer.

Other biogeochemical parameters (Table 1) were measured at these two sites during the same time period, including total organic carbon content, chlorophyll-*a* (Chl-*a*) profiles, macrofauna abundance, bioturbation coefficient and oxygen uptake rate by several groups at Marine Sciences Research Center/State University of New York at Stony Brook. Generally, annual averaged primary productivity in Long Island Sound is about 209 $gC/m^2/y$ (Riley, 1956) and there is a clear annual pattern of phytoplankton production in the Sound: high production during a late winter − early spring bloom and low production in late fall and early winter (Conover, 1956; Peterson, 1986). Water column phytoplankton and primary productivity are higher in western LIS than central LIS (Riley and Conover, 1956), resulting in a 2–12 fold higher flux of planktonic carbon to underlying sediments at station A than at station P (Sun *et al.,* 1994). A substantial difference (12×) in the organic matter flux between these two sites occurs in late winter − early spring (referred to here as the high production period).

b. Analysis of lipids

Pigment analysis for PULSE samples was done by Gerino *et al.* (1998) using the procedure as described by Sun *et al.* (1991). In brief, pigments were extracted from thawed wet sediment samples using acetone. Extracts were analyzed for pigments by HPLC.

Lipids were extracted from sediments with methylene chloride-methanol (2:1) in a Soxhlet apparatus (24 h). Solvent-extractable lipids were partitioned into the methylene chloride phase by addition of 5% NaCl solution. These extractable lipids are operationally defined as the ''free'' pool. Lipids in this extractable pool were saponified using 0.5 M KOH/MeOH; neutral lipids were then partitioned out of the basic solution (pH > 13) while acidic lipids were extracted following acidification with HCl (pH < 2) using hexane. Extracted sediment residues were subsequently saponified using 0.5 M KOH/MeOH to release ''bound'' lipids, and bound neutral and acidic compounds were extracted as above. Bound lipids are operationally defined as those associated to the sediment matrix in some manner that precludes solvent extraction but that are released by alkaline hydrolysis. Fatty

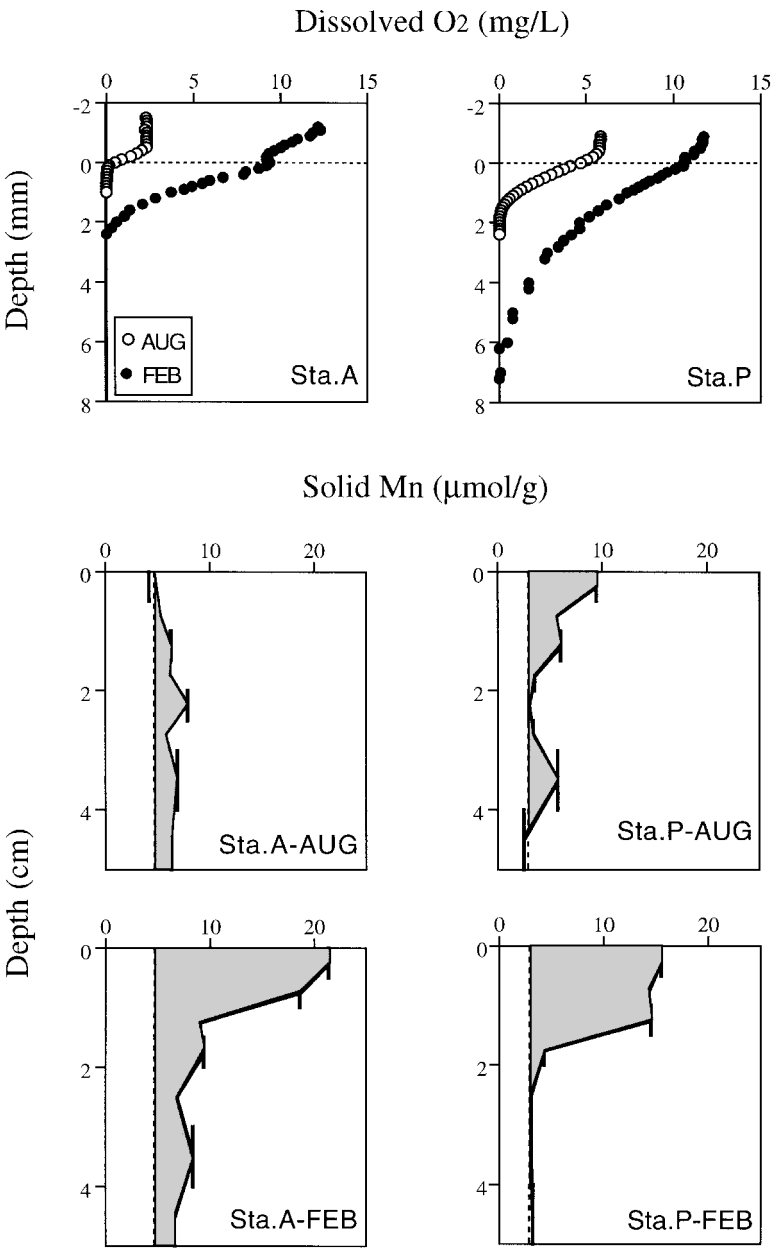

Figure 1. Dissolved oxygen and solid Mn profiles in station A and P sediments during AUG/88 and FEB/89. The shaded areas are reactive inventory of solid Mn.

Table 1. Biochemical parameters at LIS stations A and P during August-88 and February-89.

	August	*February*
Percent organic carbon (%) in surface (0–0.5 cm) sediments:*		
Station A	4.69	4.07
Station P	1.44	2.01
Reactive chlorophyll-*a* inventory (μg/cm²) in upper 10 cm sediments:*		
Station A	23.5	75.6
Station P	2.77	6.33
Macrofauna (0.5 mm) abundance (individual/m²):**		
Station A	76	506
Station P	838	453
Bioturbation coefficient (cm²/d):#		
Station A	0.15	0.03
Station P	0.37	0.03
Oxygen uptake rate (mmol/m²/d):##		
Station A	7.5	11.6
Station P	14.9	8.8

*—data from Sun *et al.* (1994).
**—data from Aller *et al.* (1991).
#—calculated from ^{234}Th data (Cochran and Hirschberg, 1991).
##—data from Mackin *et al.* (1991).

acids were methylated with BF_3-MeOH, and the resulting FAMEs extracted with hexane and isolated by silica gel chromatography (1 g activated Biosil-A; FAMEs eluted with 10% ethyl acetate in hexane). Neutral lipids were separated into different fractions (L1–L10) by adsorption chromatography (7g Biosil A, 100–200 mesh, 5% deactivated with distilled water) using a sequence of solvents of increasing polarity (Wakeham and Beier, 1991). 4-Desmethyl sterols eluted in fraction L7 (20% ethyl acetate in hexane) were treated with BSTFA in acetonitrile to form TMS-ethers.

FAMEs and sterol-TMS-ethers were analyzed by capillary gas chromatography using a Carlo Erba model GC6000 gas chromatography with an on-column injector and flame ionization detector. Separations were achieved with a 30 m × 0.25 mm i.d. column coated with 5%-phenylmethyl silicone (DB-5, J & W Scientific) operated with a linear temperature program of 100–310°C at 3°/min and with H_2 as carrier gas. Internal standards (5α(H)-cholestane for sterol-TMS-ethers and nonadecanoic acid methyl ester for FAMEs) were added to samples immediately prior to GC analysis to aid in quantification. Lipid concentrations are reported in units of μg/g dry sediment. Selected samples were analyzed by gas chromatography-mass spectrometry to identify components of interest. GC-MS was performed on a Hewlett-Packard 5890/Finnigan Incos 50 GC-MS system using the same

Table 2. Major fatty acids and sterols in LIS plankton and sediments.

Fatty acids	Sterols	Sterol shorthand notation
i-14:0*	24-nor-cholesta-5,22E-dien-3β-ol	$26\Delta^{5,22}$
14:0	24-nor-cholest-22-en-3β-ol	$26\Delta^{22}$
i-15:0	cholesta-5,22E-dien-3β-ol	$27\Delta^{5,22}$
a-15:0	5α(H)-cholest-22-en-3β-ol	$27\Delta^{22}$
15:0	cholest-5-en-3β-ol	$27\Delta^{5}$
i-16:0	5α(H)-cholestan-3β-ol	$27\Delta^{0}$
16:1(ω9)	cholesta-5,24E-dien-3β-ol	$27\Delta^{5,24}$
16:1(ω7)	24-methylcholesta-5,22E-dien-3β-ol	$28\Delta^{5,22}$
16:1(ω5)	24-methyl-5α(H)-cholest-22-en-3β-ol	$28\Delta^{22}$
16:0	24-methylcholesta-5,24(28)-dien-3β-ol	$28\Delta^{5,24(28)}$
17:0	24-methylcholest-5-en-3β-ol	$28\Delta^{5}$
18:4(ω3)	24-methyl-5α(H)-cholest-24(28)-en-3β-ol	$28\Delta^{24(28)}$
18:2(ω6)	24-methyl-5α(H)-cholestan-3β-ol	$28\Delta^{0}$
18:1(ω9)	23, 24-dimethylcholesta-5,22E-dien-3β-ol	$29\Delta^{5,22}$-dimethyl
18:1(ω7)	24-ethylcholesta-5,22E-dien-3β-ol	$29\Delta^{5,22}$-ethyl
18:0	24-ethyl-5α(H)-cholest-22-en-3β-ol	$29\Delta^{22}$
20:5(ω3)	23, 24-dimethylcholest-5-en-3β-ol	$29\Delta^{5}$-dimethyl
24:0	24-ethylcholest-5-en-3β-ol	$29\Delta^{5}$-ethyl
	24-ethyl-5α(H)-cholestan-3β-ol	$29\Delta^{0}$
	24-ethylcholesta-5,24(28)Z-dien-3β-ol	$29\Delta^{5,24(28)}$
	24-ethyl-5α(H)-cholest-24(28)Z-en-3β-ol	$29\Delta^{24(28)}$

i = *iso*-branched; *a* = *anteiso*-branched.
*Carbon number:number of double bonds.

type of column as for GC analysis except with He as carrier gas. Operating conditions were: mass range 50–650 with a 1 s cycle time; 70 eV ionizing energy; GC temperature program 80–150°C at 20°/min followed by 150–320°C at 4°/min and a 15 min hold at 320°C.

3. Results

a. Time-dependent variations of fatty acids and sterols in surface sediment of LIS—the PULSE experiment

Surface sediment samples (top 0–0.5 cm) were analyzed for fatty acids and sterols during the 200-day PULSE experiment. Major fatty acids (18 compounds) and 4-desmethylsterols (21 compounds) were quantified (Table 2). Water column Chl-*a* concentrations during the PULSE experiment (Fig. 2a; Gerino *et al.,* 1998) showed a bloom during April 1993 (between sediment sampling periods 6 and 7). A peak in Chl-*a* concentration (Fig. 2b; Gerino *et al.,* 1998) also occurred in the surface sediment in the 7th sample (collected 10 days after the bloom), with a Chl-*a* concentration 4-fold higher than that in pre-bloom sediments. Surface (0–0.5 cm) sediment organic carbon content (Fig. 2c; Popp, personal communication) increased ~15% as a result of the bloom.

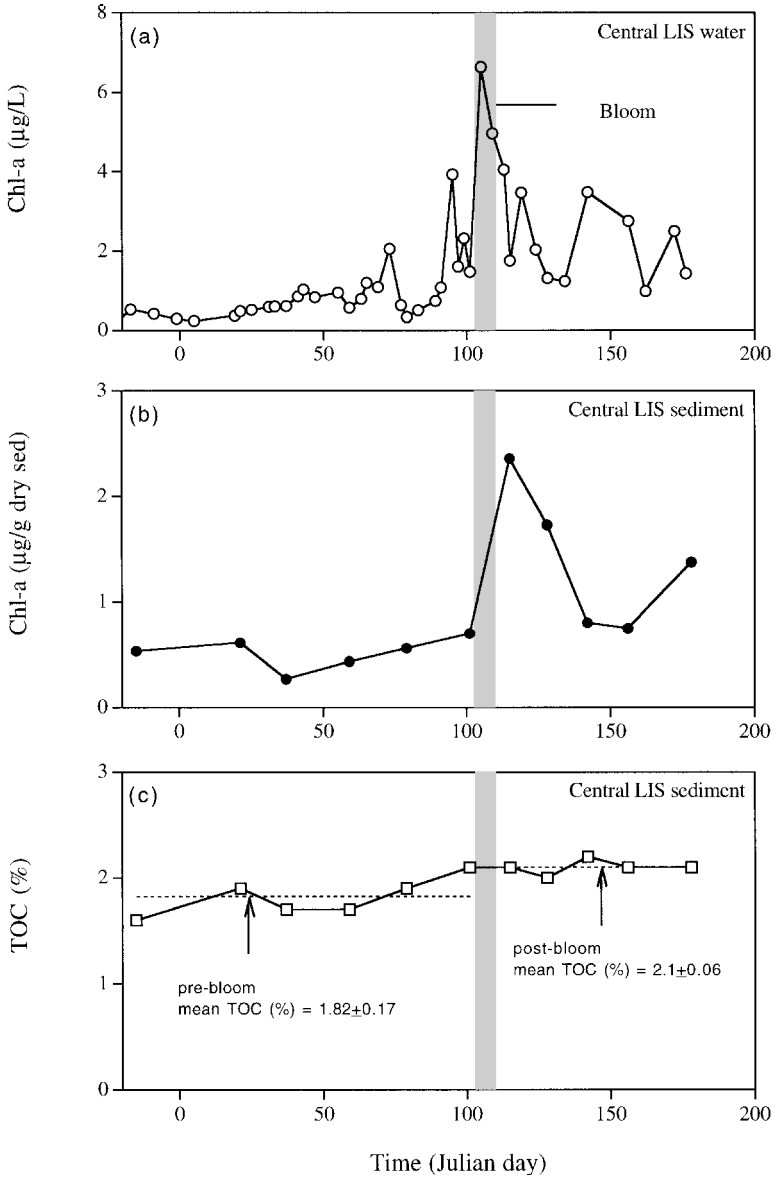

Figure 2. (a) Variations in concentration of chlorophyll-*a* in central LIS surface water during 200-day PULSE sampling period (3–4 day interval); (b) variations in concentration of chlorophyll-*a* in top 0–0.5 cm sediment samples during PULSE sampling period (2 week interval); (c) variations in total organic carbon percent (%) in top 0–0.5 cm sediment samples during PULSE sampling period. Note that gray bars in the figure represent the bloom period.

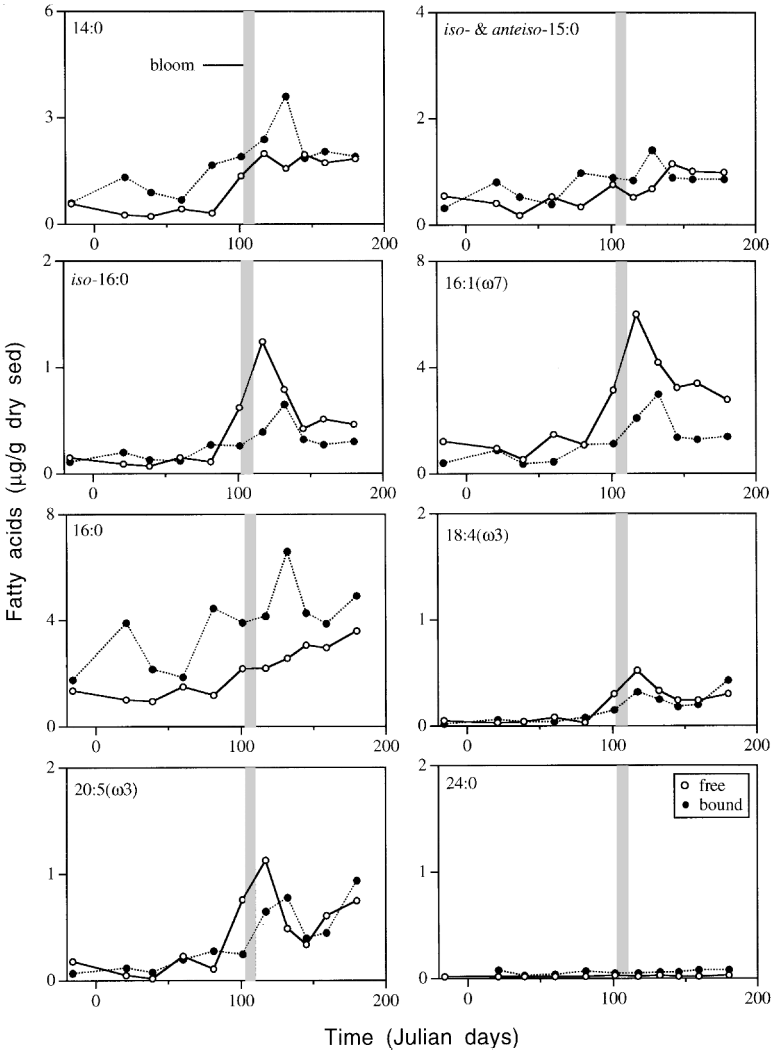

Figure 3. Variations in concentration of free and bound fatty acids in central LIS surface sediments (top 0.5 cm) during 200-day PULSE sampling period.

Concentrations of many fatty acids (Fig. 3) and sterols (Fig. 4) in surface sediments varied over the bloom. Several free unsaturated acids such as 16:1(ω7), 18:4(ω4), and 20:5(ω3) clearly increased in concentration immediately following the bloom and then subsequently decreased, consistent with the pattern for Chl-*a*. Most branched acids (i.e., *iso*-14:0, *iso*- and *anteiso*- 15:0) showed little change with time, an exception being free *iso*- 16:0 that followed Chl-*a* pattern. Free 14:0 and 16:0 acids continuously increased in concentration throughout the bloom and had not yet begun to decrease by the end of the sampling period. These saturated fatty acids were more abundant in the bound than in the

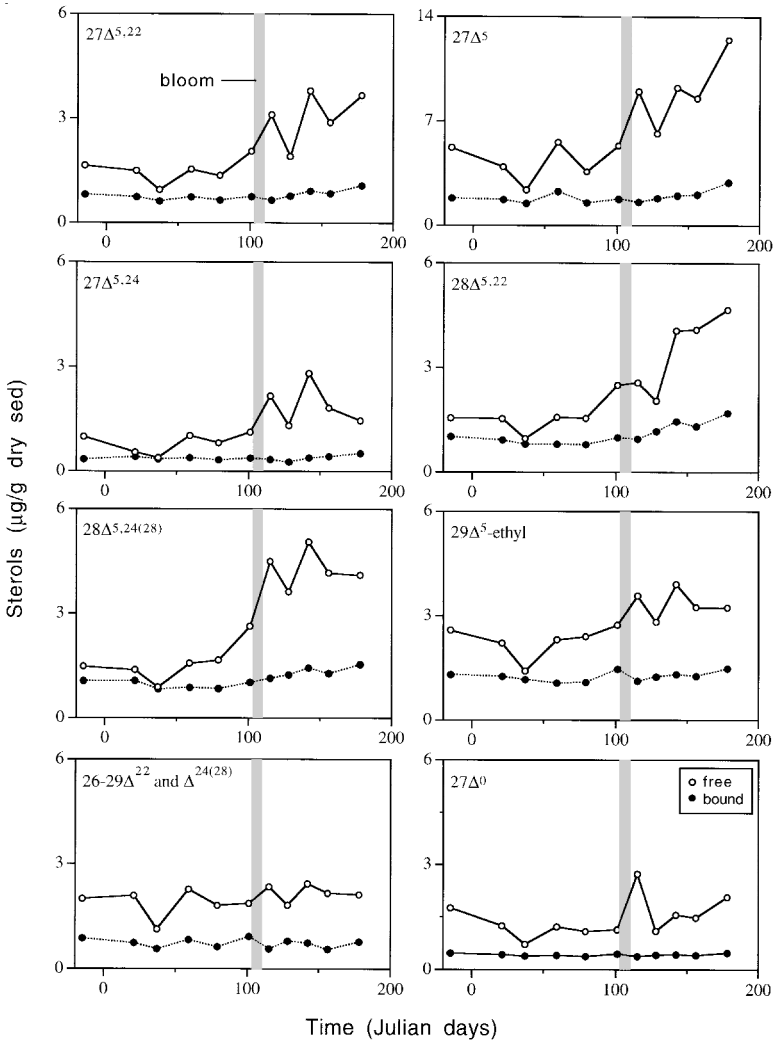

Figure 4. Variations in concentration of free and bound 4-desmethyl sterols in central LIS surface sediments (top 0.5 cm) during 200-day PULSE sampling period.

free pool. For some saturated and unsaturated fatty acids, including 16:1(ω9), 16:1(ω5), 17:0, 18:2(ω6), 18:1(ω9), 18:1(ω7), 18:0, and 24:0, the free and bound concentrations were relatively unchanged over the entire sampling period.

Free sterols were consistently more abundant and showed greater variability in concentration than the bound sterols. Temporal variations in free sterol concentrations were greater than for fatty acids. Concentrations of cholesterol and C_{26}–C_{28} diunsaturated sterols (e.g., 24-nor-cholesta-5,22E-dien-3β-ol, cholesta-5,22E-dien-3β-ol, cholesta-5,24E-dien-3β-ol, 24-methylcholesta-5,22E-dien-3β-ol, and 24-methylcholesta-5,24(28)-dien-3β-ol),

all of which are planktonic in origin, continued to increase until the end of the sampling period, long after the bloom had subsided. Most C_{29} sterols showed lower variations in concentration over the sampling period. Side-chain monounsaturated sterols (26–29Δ^{22}) and fully saturated sterols (27–29Δ^{0}) generally showed little variability during the 200-day sampling period except for 5α(H)-cholestan-3β-ol, which had a sharp peak in concentration after the bloom.

b. Depth-dependent variations of fatty acids and sterols in LIS sediments

Fatty acids and sterols can be divided into several subclasses according to structural characteristics (e.g., saturated vs. unsaturated, branched vs. normal, short chain vs. long chain, and ring-unsaturated vs. side chain unsaturated). The concentrations of these subclasses varied with depth at each of the two sites and temporally (Table 3 and 4). Concentrations of most fatty acids and sterols, except for the 24:0 acid and ring and fully saturated sterols, decreased by 2–10 fold in upper 5 cm sediments. Generally, greater variation in concentration with depth was observed for free than bound fatty acids and sterols. Thus, we will focus on the diagenesis of free fatty acids and sterols in this study.

Depth-dependent distributions of summed free fatty acids and sterols (Fig. 5) varied differently at the two sites (stations A and P) and between the two sampling periods (AUG and FEB). In AUG, free fatty acids and sterols in surface sediments were ~10-fold more abundant at station A than at station P. Concentrations gradually decreased with depth (although there was a marked subsurface maximum in the fatty acid profile) at station A while relatively uniform concentrations were observed throughout the core at station P. In FEB, little change in free fatty acid and sterol concentrations were observed with depth at station A while significant concentration gradients occurred at station P. The fatty acid and sterol profiles at station P were similar to those of Chl-*a* during two sampling periods. In contrast, the profiles of fatty acids and sterols at station A were markedly different from Chl-*a* profiles during AUG and FEB.

Vertical distributions for selected fatty acids in LIS sediments, at the two sites and for the two seasons, are shown in Figure 6. Generally, surface concentrations of these fatty acids were similar at both sites in FEB but were quite different (~3–10× higher at station A relative to station P) in AUG. Furthermore, the shapes of depth profiles of these fatty acids were quite different in AUG: low and relatively invariant concentrations occurred throughout the core at station P but very high concentrations with several subsurface maxima at station A. Several fatty acids (e.g., 14:0, *iso*-16:0, 16:1(ω7), 18:4 (ω3) and 20:5(ω3)) had high concentrations in surface (0–0.5 cm) sediment and decreased exponentially with depth at both sites during FEB. This trend was similar to that of Chl-*a*, suggesting that phytoplankton are a major source of these fatty acids to sediments during the bloom period. Depth-related gradients of these fatty acids were relatively greater at station P than at station A. Palmitic acid (16:0) had a small down-core concentration gradient at station P but almost no gradient at station A in FEB, implying that the distribution of this fatty acid does not necessarily depend on the direct contribution from plankton even if it is one of the

most abundant fatty acid in phytoplankton and zooplankton. Benthic organisms, including fauna and bacteria, may be a second major source of 16:0 in sediments (Farrington *et al.,* 1973; Parrish *et al.,* 1996; Perry *et al.,* 1979). Branched *iso-* and *anteiso*-15:0 and long-chain 24:0 showed little gradient in profile at stations A and P in FEB, indicating that these fatty acids are not related to the bloom inputs and consistent with their bacterial and vascular plant sources, respectively.

Profiles of several sterols also showed different trends at the two sites and during two seasons (Fig. 7). In FEB, $27\Delta^5$, $29\Delta^5$-ethyl, and most diunsaturated sterols ($\Delta^{5,22}$ and $\Delta^{5,24(28)}$) except for $27\Delta^{5,24}$ showed apparent concentration gradients at both sites, consistent with Chl-*a* and phytoplankton-derived fatty acids, implying a phytoplankton source for these sterols. Cholestanol ($27\Delta^0$) and side-chain unsaturated sterol ($27\Delta^{22}$) had a relatively weak concentration gradient at station P while the concentrations of these stanols increased slightly with the depth at station A. In AUG, the concentrations of these sterols were very low and invariant with depth at station P relative to station A. However, some sterols showed different profile shapes at station A during AUG. For example, $27\Delta^5$, $27\Delta^{5,22}$ and $28\Delta^{5,24}$ had clear concentration gradients while $27\Delta^{22}$, $27\Delta^0$ had weak or non-existent gradients. Several sterols displayed subsurface maxima in the upper 5 cm sediments. Although concentrations of $27\Delta^{5,24}$, $28\Delta^{5,24(28)}$ and $29\Delta^5$-ethyl were higher in the upper 5 cm sediments than in deep ($<$5 cm) sediments, several subsurface maxima were observed in the 0.5–1 cm and 2.5–3 cm horizons.

4. Discussion

a. Sources of sedimentary fatty acids and sterols

There are many potential sources of organic matter in coastal sediments, and fatty acids and sterols have been used to evaluate sources of organic matter in various depositional environments (Volkman, 1986; Wakeham and Lee, 1993). One of the major purposes of this study was to evaluate how a seasonal phytoplankton bloom impacts sedimentary lipid composition. A key piece of information, therefore, is what specific fatty acids and sterols are contributed by primary producers and how are they altered by biochemical processes in the LIS water column and sediment.

Chl-*a* in the water column (Fig. 2a) showed that during the PULSE experiment the phytoplankton bloom occurred between the 6th and 7th sediment sampling periods. A large pulse of phytoplankton detritus was delivered to the underlying sediment following the bloom, as indicated by the sharp Chl-*a* peak in surface sediment 10 days after the bloom (Fig. 2b). With the settling of plankton detritus, sedimentary organic carbon content increased $\sim$15% relative to that prior to the bloom (Fig. 2c). This pulse of detritus also resulted in significant increases in concentrations of certain fatty acids and sterols in the sediment. There were two trends in concentration increases following the bloom. One closely followed the pattern of Chl-*a*, with a sharp peak at the PULSE 7 sampling, while the second trend was a continual increase until the end of the PULSE sampling (PULSE 11), two months after the bloom. Among fatty acids, 16:1(ω7), 18:4(ω4) and 20:5(ω3), and

Table 3. Concentration (μg/g dry sed.) data for selected fatty acid classes from LIS stations A and P cores (AUG-88 and FEB-89).

Depth (cm)	0–0.5	0.5–1	1–1.5	1.5–2	2–2.5	2.5–3	3–4	4–5	5–7	7–10
LIS Station A (AUG-88)—free fatty acids										
branched	18	37	29	13	9.1	15	14	9.1	3.3	0.84
C_{14}–C_{18} sat	69	120	75	31	21	45	36	25	9.7	3.1
C_{16}–C_{18}-monounsat	49	79	58	25	21	34	38	26	8.2	1.1
C_{18}–C_{20}-polyunsat	11	17	6.5	3.6	3.7	3.8	5.1	3.5	1.3	0
C_{24}-sat	0.27	0.2	0.2	0.19	0.1	0.11	0.1	0.05	0.07	0.08
total fatty acids	150	250	170	72	56	98	92	63	23	5.1
LIS Station A (AUG-88)—bound fatty acids										
branched	4.6	15	6.8	9.4	10	9.3	9.1	6	5.9	6.5
C_{14}–C_{18}-sat	30	77	33	45	47	44	39	27	26	26
C_{16}–C_{18}-monosat	10	27	13	19	26	23	21	12	11	8.9
C_{18}–C_{20}-polysat	1.8	4.3	2	2.8	4.2	3.2	3	1.4	1.4	1.2
C_{24}-sat	0.33	0.63	0.17	0.35	0.53	0.17	0.16	0.2	0.35	0.19
total fatty acids	46	120	55	76	88	79	73	46	44	43
LIS Station P (AUG-88)—free fatty acids										
branched	1.2	1.9	1.4	1.5	1.4	2.4	1.1	1	0.48	0.54
C_{14}–C_{18}-sat	3.9	6.3	4	4.1	3.2	8.1	3.3	2.3	1	1.1
C_{16}–C_{18}-monosat	3.3	4.8	2.7	3.1	2.6	5.9	2	1.6	0.7	0.54
C_{18}–C_{20}-polysat	0.62	1.2	0.42	0.76	0.39	0.83	0.34	0.17	0.09	0.03
C_{24}-sat	0.03	0.05	0.03	0.02	0.03	0.03	0.04	0.01	0.01	0.01
total fatty acids	9	14	8.5	9.5	7.6	17	6.7	4.9	2.3	2.2
LIS Station P (AUG-88)—bound fatty acids										
branched	3.5	2.4	3.1	2.7	2.4	1.8	1.8	1.8	1.9	1.6
C_{14}–C_{18}-sat	16	14	12	10	9.9	8.8	8.3	8.1	7.4	6.6
C_{16}–C_{18}-monosat	6.6	6.6	4.8	4.3	4.1	2.3	2.1	2.2	2.2	1.4
C_{18}–C_{20}-polysat	1.2	3.1	1.1	0.98	1	0.89	0.67	0.67	0.48	0.24
C_{24}-sat	0.09	0.15	0.07	0.04	0.13	0.13	0.12	0.1	0.2	0.14
total fatty acids	27	26	21	18	18	14	13	13	12	10
Depth (cm)	0–0.5	0.5–1	1–1.5	1.5–2	2–3		3–4	4–5	5–7	7–10
LIS Station A (FEB-89)—free fatty acids										
branched	6.4	5.6	6.8	3.8	6.1		6.5	3.8	2.8	3.8
C_{14}–C_{18}-sat	21	15	13	9.4	12		11	6	4.2	6.8
C_{16}–C_{18}-monosat	22	16	18	12	14		13	7.9	5	8
C_{18}–C_{20}-polysat	6.5	5	4	6	2.4		2.2	1.2	0.7	1.1
C_{24}-sat	0.06	0.1	0.17	0.29	0.05		0.31	0.1	0.07	0.24
total fatty acids	56	42	42	32	35		33	19	13	20

Table 3. (Continued)

Depth (cm)	0–0.5	0.5–1	1–1.5	1.5–2	2–3	3–4	4–5	5–7	7–10
LIS Station A (FEB-89)—bound fatty acids									
branched	2.4	2.3	2.2	1.5	2	2.3	3.6	3.3	4.3
C_{14}–C_{18}-sat	13	13	12	8.6	11	11	19	15	20
C_{16}–C_{18}-monosat	4.3	5	3.9	3.5	4	3.9	6.4	5.9	6
C_{18}–C_{20}-polysat	1.1	0.91	0.89	0.5	0.48	0.42	0.63	0.61	0.7
C_{24}-sat	0.11	0.12	0.14	0.11	0.11	0.09	0.15	0.12	0.1
total fatty acids	21	22	19	14	18	18	30	25	31
LIS Station P (FEB-89)—free fatty acids									
branched	5.3	2	2.4	0.94	1.3	0.72	0.6	0.4	0.24
C_{14}–C_{18}-sat	19	4.1	3.8	1.5	2	1.1	1	0.75	0.49
C_{16}–C_{18}-monosat	20	5.2	4.1	1.6	2.5	0.97	0.68	0.31	0.24
C_{18}–C_{20}-polysat	4	1.7	0.95	0.29	0.24	0.13	0.16	0.06	0.05
C_{24}-sat	0.1	0.07	0.07	0.03	0.03	0.02	0.02	0.01	0.02
total fatty acids	48	13	11	4.3	6.1	2.9	2.5	1.5	1
LIS Station P (FEB-89)—bound fatty acids									
branched	1.4	0.38	1.8	0.75	1.5		1.1	1.3	1.2
C_{14}–C_{18}-sat	8.9	1.9	9.3	4.8	7.4		5.4	5.8	5.4
C_{16}–C_{18}-monosat	0.67	0.49	2	0.36	1.5		1.1	1	0.78
C_{18}–C_{20}-polysat	0.21	0.14	0.47	0.14	0.42		0.27	0.28	0.28
C_{24}-sat	0.11	0.03	0.07	0.04	0.09		0.05	0.04	0.09
total fatty acids	11	3	14	6.1	11		7.9	8.4	7.7

iso-16:0 followed the Chl-*a* pattern, while 14:0 and 16:0 followed the trend of continuous concentration increase (Fig. 3). Trends for other fatty acids were less variable over the bloom period. Among sterols, cholesterol ($27\Delta^5$) and most C_{26}–C_{28} diunsaturated ($\Delta^{5,22}$, $\Delta^{5,24}$ and $\Delta^{5,24(28)}$) sterols followed the continuous increase trend while ring saturated sterols (Δ^{22}) varied little over the PULSE experiment period (Fig. 4). Cholestanol ($27\Delta^0$) had a sharp peak during the bloom, following the trend of Chl-*a*. C_{29} sterols except $29\Delta^{5,24(28)}$ exhibited relatively little variation relative to C_{26}–C_{28} sterols over the bloom period.

Comparison of temporal variability between sedimentary Chl-*a* and fatty acids and sterols over the bloom period provides some insight as to lipid sources. Fatty acids following the Chl-*a* trend (16:1(ω7), 18:4(ω3) and 20:5(ω3)) are derived primarily from phytoplankton, as these fatty acids are major lipids in many species of diatom (Volkman *et al.,* 1989; Dunstan *et al.,* 1994), including those that dominate the phytoplankton community during the spring bloom in LIS (Tantichodok, 1989). Although diatoms contain some diunsaturated sterols (e.g., $27\Delta^{5,22}$, $28\Delta^{5,22}$ and $28\Delta^{5,24(28)}$, Volkman, 1986), none of these sterols showed a trend similar to Chl-*a*. This implies that other sources in addition to phytoplankton may be important for these sterols.

Table 4. Concentration (μg/g dry sed.) data for selected sterol classes from LIS stations A and P cores (AUG-88 and FEB-89).

Depth (cm)	0–0.5	0.5–1	1–1.5	1.5–2	2–2.5	2.5–3	3–4	4–5	5–7	7–10
LIS Station A (AUG-88)—free sterols										
diunsaturated	120	140	88	76	60	78	57	48	28	21
ring-monounsat	160	150	72	50	43	52	40	39	23	20
side-monounsat	25	34	24	16	12	19	13	15	9.3	7.5
saturated-stanol	16	26	17	15	11	17	11	14	11	10
total sterols	320	350	200	160	130	170	120	120	71	58
LIS Station A (AUG-88)—bound sterols										
diunsaturated	10	15	8.1	22	50	22	30	13	23	15
ring-monounsat	8.1	12	6	16	38	15	21	9.4	17	11
side-monounsat	1	1.8	0.9	2.4	8.5	2.9	5.2	1.7	4.5	3
saturated-stanol	1.4	2.3	1.2	3.2	9.1	3.4	5.7	2.2	5.5	3.4
total sterols	21	31	16	43	110	43	63	26	51	33
LIS Station P (AUG-88)—free sterols										
diunsaturated	5.9	8.6	7.2	6.3	4.5	13	3.5	10	3.7	2.3
ring-monounsat	5.4	9.3	6	6.3	3.8	11	3.3	16	3.5	2.4
side-monounsat	1.2	1.7	1.5	1.4	1.1	2.7	1	2.8	1	0.68
saturated-stanol	0.95	1.5	1.5	1.4	1.2	2	1.1	3.2	1.2	0.86
total sterols	13	21	16	16	11	29	8.9	31	9.4	6.2
LIS Station P (AUG-88)—bound sterols										
diunsaturated	18	13	16	17	10	10	6.3	7.3	4.3	3
ring-monounsat	13	14	12	14	5.7	7.4	4	5.3	2.1	2.2
side-monounsat	2.5	2.1	2.6	2.9	2	1.7	1	1.3	0.98	0.5
saturated-stanol	3	1.9	3.3	3	2.1	1.8	1.1	1.4	0.8	0.59
total sterols	36	30	34	37	20	21	12	15	8.2	6.2

Depth (cm)	0–0.5	0.5–1	1–1.5	1.5–2	2–3	3–4	4–5	5–7	7–10
LIS Station A (FEB-89)—free sterols									
diunsaturated	27	26	25	25	27	27	23	21	16
ring-monounsat	26	23	20	20	23	23	18	16	13
side-monounsat	4.4	4.9	5	5.2	6.7	7.5	6	6.5	6
saturated-stanol	5.1	5.6	6	5.8	7.1	7.9	6.3	7	6.8
total sterols	62	60	56	56	64	65	54	51	41
LIS Station A (FEB-89)—bound sterols									
diunsaturated	4.6	5	5.7	5.4	5.5	7.6	5.6	6.5	4.8
ring-monounsat	3.4	3.7	4.2	4.1	4	5.4	4	4.8	3.6
side-monounsat	0.69	0.7	0.68	0.68	0.61	0.82	0.65	0.76	0.61
saturated-stanol	0.82	0.85	0.89	0.91	0.82	1.11	0.8	0.91	0.81
total sterols	9.5	10	12	11	11	15	11	13	9.9

Table 4. (Continued)

Depth (cm)	0–0.5	0.5–1	1–1.5	1.5–2	2–3	3–4	4–5	5–7	7–10
LIS Station P (FEB-89)—free sterols									
diunsaturated	15	11	8.5	5.6	4.1	3	3.3	2	1.9
ring-monounsat	15	12	7	4.4	2.8	2.2	2.8	2.2	1.5
side-monounsat	2.4	2	2.1	1.6	0.95	0.87	0.69	0.51	0.5
saturated-stanol	3.6	2.4	2.2	1.6	1.3	0.94	1.1	0.64	0.62
total sterols	36	27	20	13	9.1	7.1	7.9	5.4	4.5
LIS Station P (FEB-89)—bound sterols									
diunsaturated	2.8	2	3.3	3.1	4.1	4.4	3.1	3.2	3
ring-monounsat	2.4	1.6	2.4	2.2	2.9	3.1	2.2	2.2	2
side-monounsat	0.38	0.28	0.39	0.37	0.55	0.6	0.47	0.41	0.46
saturated-stanol	0.6	0.38	0.54	0.52	0.68	0.73	0.59	0.52	0.54
total sterols	6.2	4.2	6.6	6.2	8.2	8.8	6.4	6.4	6

Fatty acids and sterols which show a continuous increase trend probably originate from multiple sources, including phytoplankton, zooplankton and benthic fauna. Saturated 14:0 and 16:0 fatty acids exist in phytoplankton, zooplankton and fecal pellets (Volkman, 1989; Harvey *et al.,* 1987). Although some diunsaturated sterols (e.g., $27\Delta^{5,22}$ $28\Delta^{5,22}$, and $28\Delta^{5,24(28)}$) are present in phytoplankton (Volkman, 1986), they also often exist in zooplankton and their feces (Gagosian *et al.,* 1983; Harvey *et al.,* 1987). Cholesterol ($27\Delta^{5}$) is generally thought to originate mainly from zooplankton lipids (Gagosian *et al.,* 1983) and zooplankton fecal pellets are an important source to the sediments (Prahl *et al.,* 1984). Cholesterol is also present in some phytoplankton lipids (Volkman, 1986). Following the bloom, concentrations of planktonic fatty acids and sterols in the surface sediments start to increase due to a pulsed input of phytoplankton detritus. After the bloom subsided, the continued increase of some fatty acids and sterols can be partly attributed to inputs related to zooplankton grazing. Phytoplankon-derived fatty acids and sterols and zooplankton-derived cholesterol can be transported to the sediments in fecal pellets of grazers. The general relationship between phytoplankton and zooplankton in LIS water was observed by Peterson (1986): zooplankton abundance gradually increases after the phytoplankton bloom and reaches the maximum 1–2 months after the bloom.

Another source for these sterols may be linked with the temporal variation of benthic faunal abundance. Benthic animals typically contain abundant sterols (e.g., $27\Delta^{5}$, $27\Delta^{5,22}$, and $28\Delta^{5,22}$) in their tissues and feces (Yasuda, 1978; Canuel *et al.,* 1995), and animals can contribute a range of their endogenous sterols to fecal matter (Bradshaw *et al.,* 1989; Bradshaw and Eglinton, 1993). Abundances of meiofauna in the PULSE sediment samples peak (increasing from 300 to 1200/cm^2) in the PULSE 9 sampling period (37 days after the bloom) and macrofauna start to increase between the PULSE 9 (5000/m^2) and PULSE 11 (20000/m^2) (Aller, personal comm.). Recent laboratory simulation experiments (Sun and

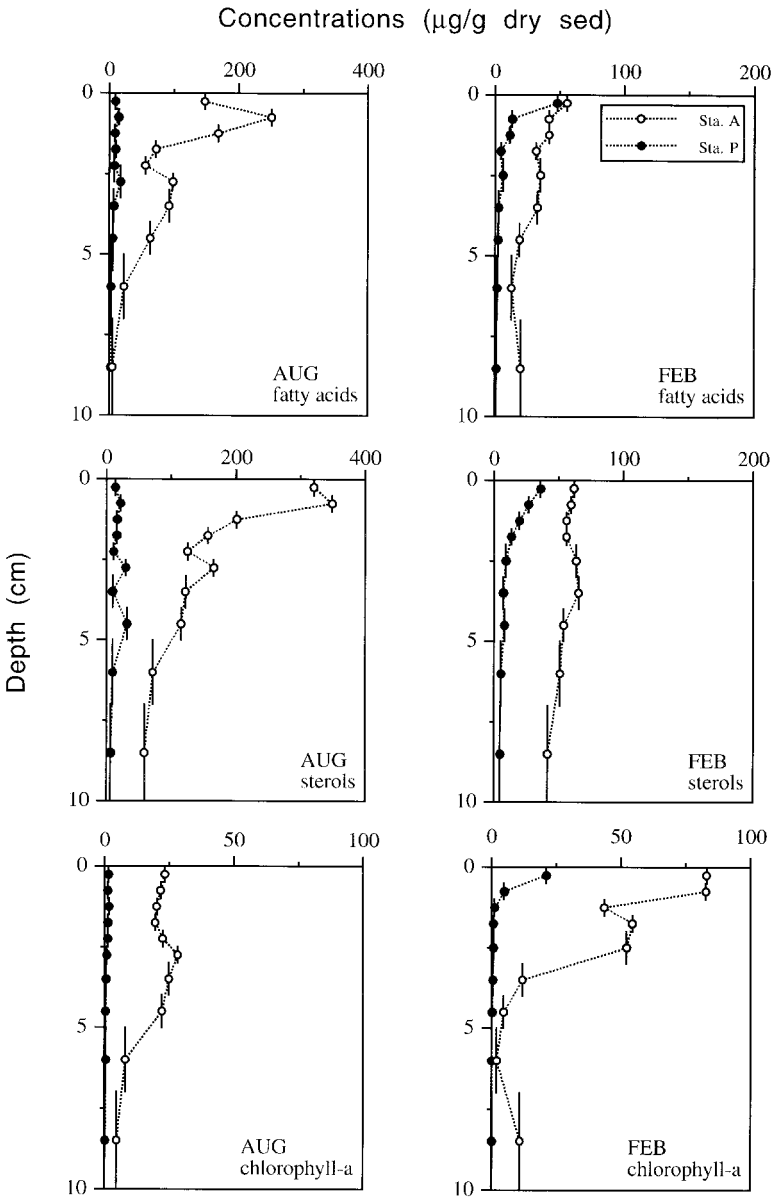

Figure 5. Depth profiles of total free fatty acids, free sterols, and chlorophyll-*a* at LIS station A (western) and P (central) during AUG/88 and FEB/89. Chl-*a* data from Sun *et al.* (1994).

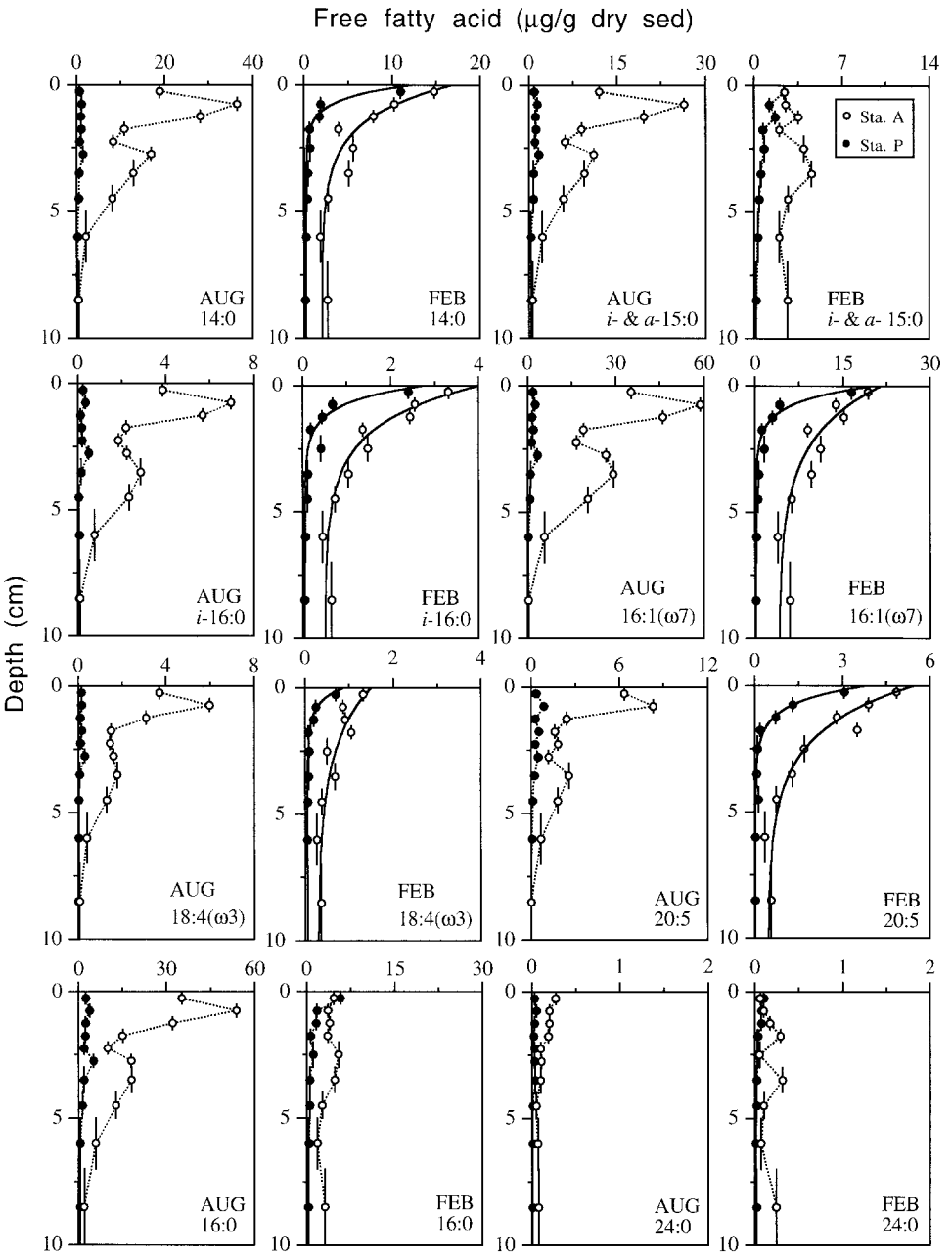

Figure 6. Depth profiles of several individual free fatty acids at LIS station A (western) and P (central) during AUG/88 and FEB/89. The solid lines are fits of a simple transport-reaction model and the dashed lines are used only to facilitate viewing.

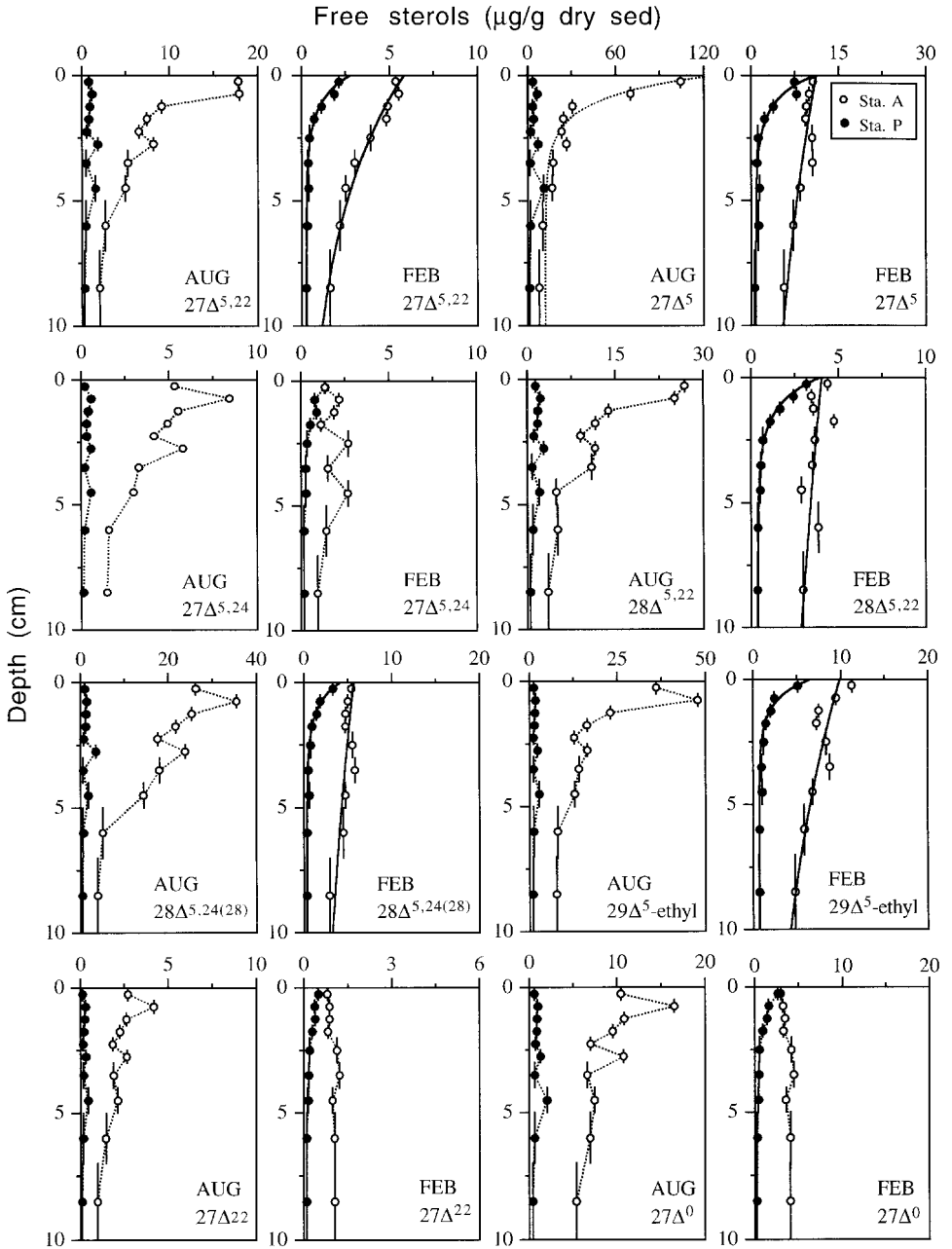

Figure 7. Depth profiles of several individual free 4-desmethyl sterols at LIS station A (western) and P (central) during AUG/88 and FEB/89. The solid lines are fits of a simple transport-reaction model and the dashed lines are used only to facilitate viewing.

Wakeham, 1998) have also shown an increase in cholesterol concentration when meiofauna migrated into experimental sediments from the surrounding sediment bed.

b. Diagenetic processes affecting distributions of fatty acids and sterols

After deposition of planktonic detritus at the seafloor, diagenesis rapidly changes the composition and concentration of organic matter. In LIS, intense diagenesis occurs in the upper 5 cm of the sediments, as shown by depth distributions of labile organic compounds (Chl-*a*, Sun *et al.,* 1991; 1994) and short-lived radionuclies (^{234}Th, Aller and Cochran, 1976; Cochran and Hirschberg, 1991; Gerino *et al.,* 1998). Diagenetic processes that affect lipid distributions in LIS sediments include particle reworking due to bioturbation, and lipid degradation due to digestion of planktonic organic matter by benthic fauna, microbial decomposition, and abiotic reactions. These processes are significantly affected by environmental redox conditions. Here, we examine important processes affecting planktonic lipid fate by comparing the lipid profiles at two sites characterized by distinct seasonal differences in redox conditions and carbon inputs.

Lipids exist in sediments as free and bound forms. In the water column, plankton contains more free than bound lipid (free/bound ratios >3 in net-plankton samples collected during PULSE study). In surface sediments (0–0.5 cm), free lipids were also more abundant (free/bound ratios: 2.5–5 for fatty acids and 5–10 for sterols). An exception to this was observed in the core collected from station P in AUG (free/bound ratios: 0.33 for fatty acids and 0.37 for sterols) when total lipids were very low. Free compounds generally showed great variability in concentration in the upper 5 cm of the sediments, while bound compounds varied less, and then in irregular patterns, throughout 10 cm cores. Thus, free pools in surface sediments may be closely linked to inputs of fresh planktonic material from the water column. The total concentrations of free lipids decreased greatly as a result of diagenesis in the upper 5 cm of sediments (Fig. 5) while there were no corresponding increases in concentrations of bound lipids (Table 3 and 4), implying that the incorporation into bound pools may not be important over the sediment depths examined. Decreases in the ratio of free/bound lipids at depth in the cores (7–10 cm) appear to be primarily caused by selective loss of free lipid during diagenesis rather than transfer from the free to bound pool.

Profiles (Fig. 5) of summed free sedimentary fatty acids and sterols varied differently at the two sites and between seasons, implying that distributions of these compounds were controlled by different processes. The winter-spring bloom that occurred one week before the FEB sediment sampling resulted in a large pulsed input of planktonic detritus at both sites, as shown by sharp Chl-*a* gradients in surface sediments. In addition, a relatively higher inventory of reactive Chl-*a* occurred during FEB than other seasons (Sun *et al.,* 1994), also indicating the pulse input of phytoplankton detritus. However, concentration gradients in summed free fatty acid and sterol profiles were obvious only at station P. The absence of lipid concentration gradients at station A, despite higher Chl-*a*, during the

bloom may be due to relatively high free lipid "background" concentrations remaining at station A (down to 10 cm), which masked the planktonic lipid input from the bloom. In fact, typical phytoplanktonic fatty acids (e.g., 14:0, 16:1(ω7) and 20:5) and sterol ($27\Delta^{5,22}$) indeed showed the gradients at station A in FEB (Figs. 6–7). Other nonplankton fatty acids and sterols accounted for relatively large proportion of total sedimentary lipids during this time, so that no apparent concentration gradients were observed for summed fatty acids and sterols at station A. In AUG, the low primary production period, marked differences in lipid profiles were observed between stations A and P (Fig. 5). Although inputs of "fresh" phytoplanktonic carbon during summer were low (indicated by higher ratios of phaeopigments/Chl-*a* during summer than during spring, Sun *et al.,* 1994) at both sites, much larger amounts of fatty acids and sterols were present in surface sediments at station A while little was at station P. Fatty acids and sterols depositing at station A during AUG derive not only from primary producers, the phytoplankton, but also from secondary producers, zooplankton and bacteria. The difference in lipid profiles between two sites during summer is more likely caused by different degradation processes occurring at different redox conditions.

In this study, degradation is defined as net loss of free (solvent-extractable) compound, including remineralization and transformation. Phytoplankton- and zooplankton-derived 14:0, *iso*-16:0, 16:1(ω7), 18:4(ω3), 20:5, cholesterol and C_{26}–C_{28} diunsaturated sterols were preferentially degraded in the upper 5 cm sediments so that concentrations decreased to low but constant background levels below 5 cm regardless of how the inputs varied seasonally. However, due to the seasonal variations in the amount and type of planktonic material delivered to the sediment and seasonal difference in dissolved oxygen content in the bottom waters, the extent of diagenetic loss was quite different between stations A and P.

Modeling the down-core profiles of planktonic fatty acids and sterols provides a means to quantify diagenetic processes. Concentration patterns of planktonic lipids with depth in sediments are controlled by input from the overlying water column, transport due to benthic faunal mixing, and biochemical degradation (transform and remineralization); differences are due to variations in the relative importance of each process. Degradation rates must be faster than mixing because lipid concentrations decrease within the top 5 cm of the sediments. We can use a simplified one-dimensional transport-reaction model to estimate degradation rate constants, ignoring the advection term and assuming that overall degradation processes follow first-order kinetics as implied by previous field and incubation experiments (Sun *et al.,* 1993; 1997). The simplification was made based on the fact that the Peclet number (SL/D_B) is much less than 1 (Lerman, 1975; Berner, 1980). In LIS, the average S (sedimentation rate) is about 0.09 cm/yr (Kim and Bokuniewicz, 1991), D_B ranges from 0.01 to 0.4 cm^2/day (Aller *et al.,* 1980; Cochran and Hirschberg, 1991), and the length scale (L) in this study is 5–10 cm, which is also corresponding to the mixed layer. The simplified transport-reaction model is:

$$\partial C/\partial t = D_B(\partial^2 C/\partial x^2) - kC \quad (1)$$

Table 5. Degradation rate constants (y^{-1}) and correlation coefficients for planktonic fatty acids and sterols derived from profile measurements during FEB in LIS sediments.

	k (sta A)	r^2	k (sta P)	r^2
Fatty acids				
14:0	5.5	0.72	34	0.78
iso-16:0	4.2	0.8	21	0.79
16:1(ω7)	3.0	0.79	24	0.95
18:4(ω3)	2.0	0.73	30	0.8
20:5(ω3)	3.0	0.92	21	0.93
Sterol				
$27\Delta^{5,22}$	0.27	0.97	8.8	0.76
$27\Delta^{5}$	0.05	0.81	7.3	0.72
$28\Delta^{5,22}$	0.012	0.33	8.4	0.8
$28\Delta^{5,24(28)}$	0.052	0.58	12	0.8
$29\Delta^{5}$-ethyl	0.071	0.79	15	0.73

where:

C = concentration of planktonic lipid compound;

t = time;

x = depth in sediment;

D_B = particle mixing coefficient;

k = degradation rate constant.

Approximating compound inventories as being at steady state after a bloom on a time scale of ~2–3 months and setting the boundary conditions as:

$$x = 0,\ C = C_0$$

$$x \rightarrow \text{large } (>5 \text{ cm}),\ C = C_B \text{ (background concentration)}$$

the solution of the above simplified equation (1) is:

$$C = (C_0 - C_B)\exp\,[-x(k/D_B)^{1/2}] + C_B. \qquad (2)$$

Because D_B estimates were known from ^{234}Th distributions on separate subcores at same site (similar assumptions were made, see Cochran and Hirschberg, 1991) collected at the same time, k values can be derived from the slope $(k/D_B)^{1/2}$ of plot ln $(C - C_B)$ vs. x.

In this study, only typical planktonic components (14:0, *iso*-16:0, 16:1(ω7), 18:4(ω3) and 20:5(ω3) fatty acids, and $27\Delta^5$ and diunsaturated sterols) were modeled for FEB profiles (solid curves in Fig. 6 and 7). Estimated k values and correlation coefficients are given in Table 5. Degradation rate constants are 5–15× higher for fatty acids, and 30–700× higher for sterols, at station P than at station A, although surface concentrations were at comparable levels. Sediment profiles of these fatty acids and sterols at both sites during this period showed trends of exponentially-decreasing concentrations (Fig. 6 and 7), but the gradients were much greater at station P than at station A. In FEB, the entire LIS water column was oxygenated and redox conditions were similar at both stations A and P

(Fig. 1). Benthic macrofaunal abundances and bioturbation rates were also similar at both sites (Table 1). When planktonic carbon flux (based on Chl-*a* inventory, Table 1) was higher at station A than at station P, benthic respiration rate was correspondingly 30% higher at station A. Several possible reasons may be considered for lower degradation rate constants for lipids at station A. First, if lipids are generally less reactive than carbohydrates and proteins in phytoplankton detritus during diagenesis (Harvey *et al.,* 1995), then the net respiration rate may mainly account for decomposition of more reactive components if the carbon flux exceeds the respiration rate as the case in station A. In contrast, if the carbon flux is less than oxygen supply rate, as is the case at station P, all components, including lipids, can be decomposed although the overall respiration rate may be lower. Second, the redox regime of the two sites varied differently: a seasonal shift from anoxic (from the previous summer) to oxic conditions in surface sediments (during winter and spring) occurred only at station A (Fig. 1), perhaps leading to a lower net efficiency for lipid degradation. Third, there were subsequently higher background concentrations of lipids at station A, which may exist in more protective matrix (e.g., association with clay minerals) and are resistant to degradation (Marshman and Marshall, 1981; Mayer, 1994). Bioturbation may mix these residual background compounds with freshly input compounds in the upper 5 cm sediments, leading to a slower apparent net degradation rate constant.

During summer, inputs of lipids from the water column decreased at both stations as primary productivity declined. Benthic processes also differed at the two sites as a function of differences in bottom water and sediment oxygen content. The occurrence of hypoxia at station A greatly reduces the abundance of aerobic macrofauna, making the mixing rate at station A ~2 fold lower than that at station P. Fatty acids and sterols were largely degraded to background levels at station P, so rate constants can not be estimated for station P from summer profiles. Degradation in AUG at station P must be very fast so as to cancel out a continuous rain of planktonic lipids. On the other hand, concentrations of 16:1(ω7), 20:5(ω3), cholesterol, and C_{26}–C_{28} diunsaturated sterols remained high in sediments at station A during summer. Subsurface concentration maxima for some compounds were present at station A, implying that planktonic fatty acids and sterols are probably mixed down by benthic fauna during the previous oxic regime. Although we cannot estimate degradation rate constants, it would seem that the lipid degradation rates were much slower at station A than at station P.

The August profile of free cholesterol ($27\Delta^5$) showed a sharp exponential decrease at station A, but was almost constant at station P (Fig. 7). The characteristic feature of the cholesterol profile at station A during summer may be attributed to a post-bloom lag in zooplankton input. Zooplankton abundance reaches its maximum about 1–2 months after the phytoplankton bloom (Peterson, 1986). When the oxygen content of bottom water and sediments has decreased and the activity of the aerobic benthos has been curtailed, cholesterol derived from zooplankton in the overlying water continues to accumulate at the sediment surface. In the case of high sedimentation rate and low mixing, subsurface concentration maxima cannot form in sediments. In contrast, continuous oxic conditions at

station P maintain intense activity of aerobic benthos, so rapid degradation of organic compounds in this sediment dominates the cholesterol profile in spite of the time lag in sedimentation of zooplankton lipids following the phytoplankton bloom.

c. Relative importance of carbon inputs vs. oxygen content on degradation and preservation of planktonic lipids in sediments

In LIS, about 30% (annually averaged) of phytoplankton carbon production is delivered to the bottom (Sun *et al.,* 1994). Organic carbon fluxes vary spatially and temporally in LIS. Western LIS sediments (e.g., station A) receive 2–12× more planktonic carbon than the central LIS sediments (e.g., station P) due to the spatial distribution of primary production (Sun *et al.,* 1994). The maximal difference (12×) in carbon flux generally occurs between the western and central LIS during the bloom and the minimal difference (2×) during the period of low primary production. Higher background concentrations of fatty acids and sterols occur in sediments at station A than station P, which in part may have resulted from the relatively higher flux from the water column at A. Thus, the flux of planktonic carbon may be an important factor controlling accumulation of lipids in surface sediments. However, markedly more fatty acid and sterol remained at station A in AUG than in FEB, while these lipids were more abundant at station P in FEB during the bloom than in AUG (Figs. 5–7). This can not be explained only by the difference in carbon flux into sediments at these two sites. Thus, factors other than carbon flux alone must contribute to the difference in lipid composition and quantity in the sediments collected during summer from these two sites.

Spatial and temporal variations in oxygen content in the water column and sediments regulate the composition and activity of benthic community. Oxygen content in the bottom water and sediment of LIS is closely linked to water circulation and the extent of organic matter degradation. In summer, a strong pycnocline limits vertical mixing and prevents renewal of bottom water O_2 (Beristain and Arnold, 1991). When organic matter flux exceeds the supply of dissolved oxygen into sediments, hypoxia or anoxia occurs. Decreasing bottom water oxygen content reduces the abundance of macrofauna and subsequently affects biochemical processes involved in lipid degradation. If organic matter rain continues and anaerobic processes do not efficiently degrade the lipids, they will accumulate in sediments during the transition period from oxic to anoxic conditions. This scenario apparently occurs at station A. Higher primary production and subsequent zooplankton grazing in the western LIS leads to a higher planktonic organic matter delivery to the station A sediments, compared with the central LIS station P. As organic matter degradation proceeds at station A, oxygen content in the sediment gradually drops to nearly zero in summer, but little secondary oxidant (e.g., reactive solid Mn) exists. Under these anoxic conditions, macrofauna abundance is greatly reduced. Even though the organic matter delivery to the sediment surface gradually decreases following the bloom into summer, planktonic lipids continue to accumulate in sediments. Prior to the onset of

summer anoxia, the aerobic benthos metabolize lipids and mix them down into the sediment. By the time the flux of planktonic matter drops and anoxic conditions prevail, subsurface maxima have developed. As oxic conditions return in winter but organic matter flux has not yet increased, planktonic lipids already in the sediment are further slowly degraded until the next bloom commences and the cycle begins anew.

A different picture emerges at station P that is oxygenated year round. The relatively low organic matter input never exceeds the supply of oxygen into the sediments. A bloom brings a pulse of fresh lipids into surface sediments, but extensive bioturbation and feeding by macrofauna and aerobic microbial degradation lead to rapid disappearance of this labile material. Although we are unable to estimate the degradation rate constants for summer profiles using the simplified model, the difference between respiration rates and organic carbon content at the two sites (Table 1) may reflect the relative magnitude of degradation rates.

Early experimental studies (Foree and McCarty, 1970; Jewell and McCarty, 1971; Otsuki and Hanya, 1972a; 1972b) showed minimal differences between the aerobic and anaerobic decomposition rates of algal materials. Field and laboratory evidence (Henrichs and Doyle, 1986; Pedersen and Calvert, 1990; Blackburn, 1991; Lee, 1992) has also suggested that anoxic decomposition of organic matter in sediments may not be intrinsically slower than oxic decomposition. However, planktonic organic matter is comprised of fractions which decompose at different rates under oxic and anoxic conditions (Westrich and Berner, 1984; Harvey *et al.,* 1995). Kristensen *et al.* (1995) found that soluble organics originating from the initial leaching and early hydrolysis of fresh plant detritus decayed at similar rates under aerobic and anaerobic conditions while structural components (e.g., lipid complexes) of aged plant detritus decayed much faster under aerobic than anaerobic conditions. Harvey and Macko (1997) showed that algal lipids decay at a significantly faster rate (2–13×) under oxic than under anoxic conditions. Experiments in our laboratory using ^{14}C-labeled fatty acids (Sun *et al.,* 1997) and ^{14}C-labeled cholesterol (Sun *et al.,* 1998) found significant differences (2–3×) in degradation rates when comparing oxic and anoxic conditions. The difference in degradation rate constants of fatty acids between oxic and anoxic conditions are even larger than 20× when algal cells (^{13}C-labeled algae) are incubated in sediments (Sun *et al.,* in prep.).

Variability in redox conditions of sediments may also affect specific degradation pathways. One example is the depth-dependent variations in ratios of Δ^0-stanol to Δ^5-stenol and Δ^{22}-ring saturated to $\Delta^{5,22}$-diunsaturated sterols (Gagosian *et al.,* 1980). The ratios of cholesterol ($27\Delta^0$)/cholesterol ($27\Delta^5$) and $26–28\Delta^{22}$)/($26–28\Delta^{5,22}$) increased with depth in the upper 5 cm sediments at both stations A and P. In FEB when redox conditions were the similar at both sites (stations A and P), the ratios of stanol to stenol increased similarly. However, in AUG when the redox conditions were different at two sites, the increase in the ratios appears to be faster at station A than at station P. Below 5 cm sediments, these ratios were almost constant in most cases.

Another example to illustrate the effect of redox on the degradation reaction of organic matter is phytol and its derivatives. We have observed different isoprenoid products were formed in LIS sediments when redox conditions varied (Sun *et al.,* 1998). For example, dihydrophytol (a reduced product of phytol degradation) was produced in FEB at the two sites when the whole water column in the Sound was oxygenated. The mechanism for dihydrophytol formation is likely via digestions of zooplankton (Prahl *et al.,* 1984) and benthic fauna (Bradshaw and Eglinton, 1993). In summer, an isoprenoid ketone (6,10,14-trimethylpentadecan-2-one) and an isoprenoid acid (4,8,12-trimethyltridecanoic acid), both of which are oxidized products of phytol, were formed in station A sediments under hypoxic conditions and low benthic faunal activity. When redox conditions are different in sediments, different end products of lipid degradation are produced. Harvey *et al.* (1986) observed that both CH_4 and CO_2 were major products of anoxic incubation while only CO_2 was produced in oxic incubation of bacterial membrane lipids. This issue is further addressed in our recent studies using ^{13}C-labeled algae as tracers in oxic and anoxic degradation experiments (Sun *et al.,* in prep.).

5. Conclusions

Diagenesis of planktonic lipids is closely coupled to seasonal variations in their input, bottom water and sediment oxygen content, and activities of benthic organisms. Differences in distributions of planktonic lipids in sediments from two sites in LIS reflect a balance between inputs from the water column and diagenetic loss. Similar distributions of planktonic lipids at two study sites during spring result from enhanced supply of planktonic lipids to the sediment-water interface, and similar bottom waters and sediment redox and benthic activity. In contrast, differences in distributions of lipids between the two sites occurred during summer when bottom waters of the western LIS were hypoxic. At the continuously-oxygenated site in central LIS, aerobic benthos reached maximum abundance and most planktonic lipids were consumed during summer. At the summer hypoxic site, the abundance of aerobic benthos was greatly reduced and planktonic lipids survived in surface sediments. Since planktonic carbon fluxes to the bottom had less difference between the two sites during summer than during spring, greater differences in distributions of planktonic lipids during summer may be much more dependent upon the redox transition than upon the flux of planktonic input.

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