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Spatial and temporal distributions of sedimentary chloropigments as indicators of benthic processes in Long Island Sound

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ABSTRACT

Regular spatial and seasonal distribution patterns of sedimentary chloropigments occurred at 19 subtidal stations located in Long Island Sound (LIS) from MAY 1988 to APR 1989. Inventories of chloropigments were higher (2–10×) in western than central LIS, mirroring patterns of phytoplankton production in surface waters. Shallow water sediments (< 25 m) received more chloropigments than deep stations (> 25 m). Lateral resuspension and redistribution of particles, as shown by ²³⁴Th inventories, are partly responsible for these patterns. Seasonal variations of Chl-*a* inventories in LIS sediments follow the production pattern in the water column: higher values occur in spring and lower values in summer and fall. A time lag (about 1–2 months) exists between maximum Chl-*a* (during early spring) and maximum phaeopigment sedimentary inventories (during late spring).

Vertical profiles of chloropigments often exhibited exponential decreases with depth, implying that degradation processes significantly affect chloropigment distributions. Based on temperature-dependent first-order decomposition rate constants, reactive Chl-*a* inventories were converted into planktonic carbon fluxes across the water-sediment interface. These agreed reasonably well (within a factor of 2) with total benthic O₂ uptake at the same sites. Particle reworking rates were estimated by using Chl-*a* profiles combined with diagenetic models of decomposition. The seasonal patterns and magnitudes of D_B (sediment mixing coefficients) derived from Chl-*a* distributions are similar (± 2 – $3\times$) to those estimated from ²³⁴Th distributions.

1. Introduction

Chlorophyll-*a* (Chl-*a*) is widely used to estimate water column phytoplankton biomass because it is the most abundant pigment component in almost all species of phytoplankton. In the water column, Chl-*a* can be converted into phaeopigments (derivatives of Chl-*a* with similar ring structures) as well as colorless residues during bacterial, viral, or autolytic cell lysis, photo-oxidation, and grazing activities by zooplankton (SooHoo and Kiefer, 1982; Shuman and Lorenzen, 1975; Hallegraeff, 1981; Welschmeyer and Lorenzen, 1985). Phaeopigments can be used as diagnostic

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indicators of physiological status, detrital content and grazing processes in natural populations of phytoplankton (Mantoura and Llewellyn, 1983). With the sinking of intact cells, fecal pellets, carcasses, and clumps of detrital particles, Chl-*a* and its major degradation products are delivered to the sea floor. After deposition, these labile chloropigments are rapidly degraded by benthic organisms and related chemical processes (Gelder and Robinson, 1980; Hawkins *et al.*, 1986; Bianchi *et al.*, 1988; Furlong and Carpenter, 1988).

The resulting sedimentary chloropigment profiles have potential use for estimating the rates of certain biogeochemical processes occurring at and just below the sediment-water interface. For example, our previous study (Sun *et al.*, 1991) described the estimation of seasonal fluxes of phytoplankton-derived organic matter to bottom sediments and benthic bioturbation rates based on Chl-*a* profiles at two sites in Long Island Sound (LIS). Furlong and Carpenter (1988) calculated the remineralization rates of phaeophorbides in Dabob Bay, Washington, sediment based on the phaeophorbide profile. These uses require detailed knowledge of decomposition rates of the compounds involved (Sun *et al.*, 1993a) or sedimentation information derived from additional tracer studies (Furlong and Carpenter, 1988).

In this study, we document the spatial and temporal distribution patterns of Chl-*a* and primary phaeopigments in sediments of a single estuarine basin, Long Island Sound, U.S.A. Based on these distribution patterns, we extend our previous pigment decomposition rate studies and transport-reaction models to examine benthic processes in the Sound as a whole. We make quantitative estimates of planktonic particulate carbon inputs resulting from seasonal biological production and consumption processes, lateral redistribution through the estuary, and vertical sediment reworking. The relationships between sedimentary Chl-*a* and individual phaeopigments are examined in the context of sources and degradation pathways of chloropigments and the decomposition rates of phaeophorbide estimated relative to Chl-*a*. Particle reworking rates derived from Chl-*a* are compared with those calculated from ²³⁴Th profiles throughout the Sound.

2. Sampling and methods

a. Study sites. Long Island Sound is a spindle-shaped part of the Atlantic coastal ocean bounded by Long Island, New York, on the south and Connecticut on the north (Fig. 1). The Sound extends approximately 150 km long from west to east and varies in width from 5 to 40 km. Water depths range to a maximum of ~100 m at the easternmost passages and average ~20 m overall. Salinity varies from ~24 to 28‰ and temperature oscillates during the year, ranging from about 2°C in FEB-MAR to about 22°C in AUG-SEP (Riley, 1956). Long Island Sound is a productive estuary, with net primary production in the range of ~209 gC/m²/y (Riley, 1956). In general, there is a clear annual pattern of phytoplankton production in the Sound: a great increase of primary production during a late winter-early spring bloom, and minimal

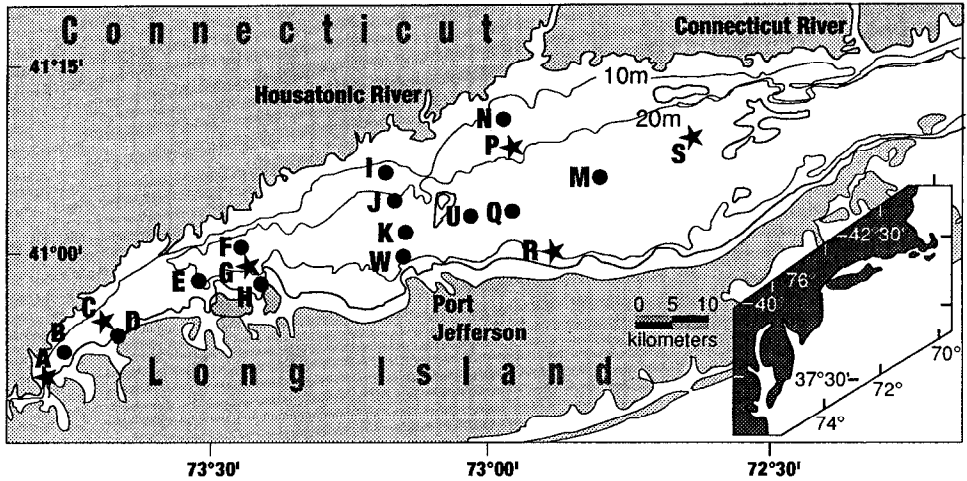


Figure 1. Sedimentary chloropigments were sampled three times each at 19 stations examined in the EPA-LISS. Samples were taken two additional times at the six reference stations (A, C, G, P, R, S).

populations in late fall and early winter (Conover, 1956; Peterson, 1986). Phytoplankton assemblages in Long Island Sound are usually dominated by diatoms except in the summer when dinoflagellates and other small phytoflagellates are abundant. Due to high turbidity during most of the year, there is no significant photosynthesis below a few meters water depth (e.g., Welsh and Eller, 1991).

The average sedimentation rate for the central and western basins is about 0.92 mm/y (Kim and Bokunicwicz, 1991) but this rate is not uniform. The greatest rates of sedimentation are in excess of 1.8 mm/y. Low rates (~ 0.3 mm/y) are found in the deep trough that runs through the central basin. Sand-size sediment is predominantly deposited in east LIS (east of $72^{\circ}40'W$) and in the nearshore area as well as in isolated shoals. Silt-clay size sediment dominates the central and western portions and covers about 60% of the total area of the Sound. Shallow stations (less than ~ 25 m) sampled during this study are generally subject to constant resuspension of surface sediment and the upper few centimeters at these stations may be eroded and redeposited during major storms (Aller and Cochran, 1976; McCall, 1978). Deeper stations (more than ~ 25 m) are also subject to resuspension, but only through tidal scour, and have considerably lower bottom turbidity than shallow stations.

b. Sampling. Sediment cores were collected from 19 stations located throughout the Sound during the EPA (Environmental Protection Agency) sponsored Long Island Sound Study (Fig. 1). In all cases, cores were obtained by using a Soutar-style box corer (surface area ~ 0.1 m²). After retrieval of a box core, the temperature in the

overlying water was recorded using a thermometer and then sub-cores of 10–20 cm length were taken by gently pushing core tubes (~ 8 cm i.d.) or rectangular acrylic corers (2.5 cm \times 10–15 cm) into the sediment. Rectangular sub-cores were first X-rayed for sediment structure and subsequently sliced, as were tube cores, into 0.5–1 cm intervals (upper 5 cm depth) or into 2–3 cm intervals (below 5 cm depth). Any effects on core depth due to compression were ignored. All subsamples were stored frozen until extraction. Seasonal sampling was carried out 5 times from MAY 1988 to APR 1989 for “reference” stations (marked by star in Fig. 1; characterized by relatively extensive biological and chemical sampling) and 3 times from MAY 1988 to NOV 1988 for the remaining stations.

c. Pigment analyses. Pigments were extracted from thawed wet sediments (~ 1 gram) using 100% acetone as described by Sun *et al.* (1991). Because the samples were frozen, the measurements given here include the total acetone-extractable pool (bound + free) as defined in our previous work. Extracts were analyzed for chloropigments by HPLC (Mantoura and Llewellyn, 1983) as modified by Sun *et al.* (1991). Identification of chloropigments in the sediment samples was confirmed by co-elution with authentic standards. Authentic Chl-*a* was obtained from Sigma Chemical Co. Phaeophytin-*a* was prepared from Chl-*a* by acidifying with HCl and phaeophorbide-*a* was prepared from a 50% acetone extract of *Skeletonema costatum* by acidifying with HCl. Pyropheophorbide-*a* was provided by Dr. Dan Repeta (WHOI). All standards were quantified spectrophotometrically (Hewlett Packard 8452 A Diode Array Spectrophotometer) using published extinction coefficients (Mantoura and Llewellyn, 1983). Peak areas were converted to concentrations using response factors calculated using the authentic standards. Replicated HPLC measurements of pigment standards (over a few months) and sediment extracts varied by $\pm 10\%$. Recovery of standard added to wet sediments was $90.6 \pm 3.1\%$ (by fluorescence) or $102.1 \pm 6.0\%$ (by UV). A total of 67 subcores were analyzed for chloropigments and analysis of duplicate cores at several stations indicated that small scale variation of pigment concentrations at a single station was within the analytical uncertainty ($\pm 15\%$). Concentrations reported here are based on fluorometric peak areas. Chloropigment concentrations are reported in units of nmol/cm³ (wet sediment; MW of Chl-*a*, phaeophorbide-*a*, pyropheophorbide-*a*, and phaeophytin-*a* = 892, 614, 556, and 870), corrected for porosity as measured by water content and assuming a particle density of 2.6 g/cm³.

3. Results

Bottom water temperature showed the expected sinusoidal variation with time (Fig. 2). Surface sediment organic carbon content (Table 1) as measured by wet oxidation (Gaudette *et al.*, 1974) decreased regularly at reference stations from west

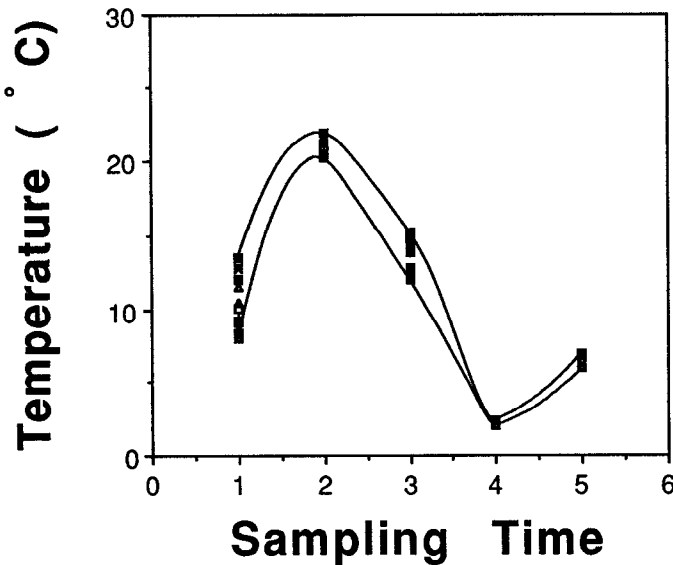


Figure 2. The bottom water temperature pattern during the 5 sampling periods at all stations (1: May–June 1988; 2: August 1988; 3: October–November 1988; 4: February 1989; and 5: April 1989).

to east, following grain size distributions and anthropogenic inputs. Seasonal surface concentrations of Chl-*a* and total identified phaeopigments (phaeophorbide-*a*, pyropheophorbide-*a*, and phaeophytin-*a*) at 6 reference stations during MAY 88 and APR 89 are compared in Figure 3. In general, several distinct features are demonstrated by the surface concentrations of chloropigments: (1) spatially, concentrations of Chl-*a* and its major phaeopigments decrease from western LIS to eastern LIS; (2) the shallow water stations (<25 m) had higher chloropigment concentrations than the deeper water stations (>25 m); (3) seasonally, concentrations of Chl-*a* and major phaeopigments were higher in spring than in summer and fall; (4) there was a time lag between high concentrations of Chl-*a* (during late winter-early spring) and major phaeopigments (during late spring).

Table 1. Percent organic carbon (% C) in surface sediments at reference stations (* indicates 0–1 cm interval, all others 0–0.5 cm).

Stations	May/June	Aug	Dec/Nov	Feb	Apr
A	4.13*	4.69	4.00	4.07	4.31
C	3.73*	3.89	3.66	3.40	3.17
G	1.38*	1.04	1.17	1.18	1.24
P	2.02*	1.44	2.46	2.01	2.28
R	1.74*	2.02	0.59	1.83	1.62
S	0.45*	0.48	0.29	1.26	0.52

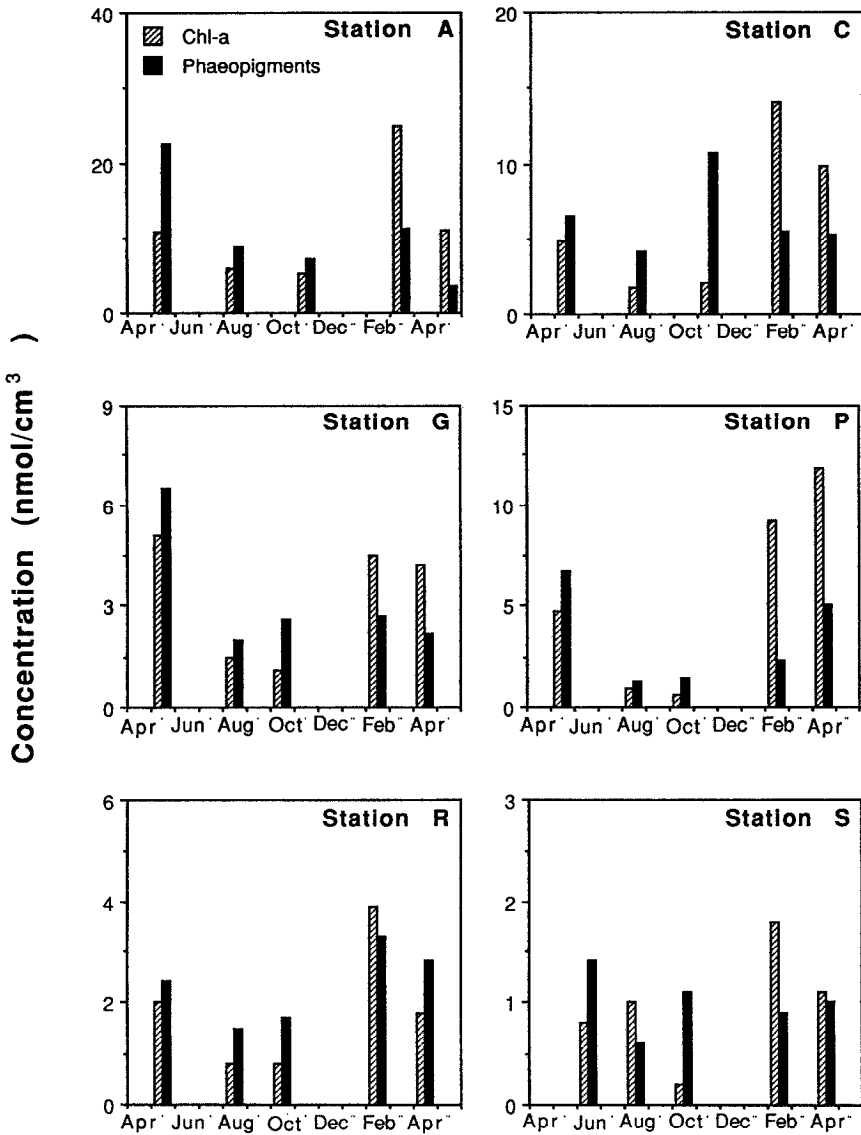


Figure 3. Comparison of surface (top 1 cm) concentrations of Chl-a (cross-hatched) and total phaeopigments (stippled) at reference stations.

The concentrations of Chl-a and major phaeopigments also varied markedly with sediment depth at each site (Fig. 4-7 show the seasonal profiles of Chl-a and individual phaeopigments at 6 reference stations). The concentrations of Chl-a at each site often decreased exponentially below the sediment-water interface and approached a lower, essentially constant, background level at depth (Table 2). For

Table 2. Chl-*a* background concentrations (nmol/cm³) in LIS sediments (~8–10 cm).

Station	Depth (m)	May/Jun	Aug	Oct/Nov	Feb	Apr
A	20.2	2.33	1.93	1.13	1.28	2.08
B	25.3	0.35	0.83			
C	18.3	0.55	0.50	0.50	0.20	1.03
D	17.5	0.54	0.21	0.33		
E	33.1	0.47	0.35	1.15		
F	25.9	0.30	0.61	0.39		
G	29.6	0.33	0.40	0.36	0.44	0.39
H	23.0	0.42	0.10	0.09		
I	11.0	0.28	0.06	0.17		
J	19.8	0.49	0.42	0.52		
K	26.9	0.13	0.21	0.07		
M	28.3	0.31	0.29	0.16		
N	10.8	0.34	0.54	0.23		
P	13.6	0.36	0.14	0.24	0.05	0.66
Q	23.6	0.09	0.12	0.27		
R	41.3	0.19	0.19	0.18	0.19	0.08
S	29.0	0.18	0.13	0.08	0.13	0.22
U	26.3	0.20	0.29	0.40		
W	38.1	0.90	0.42			

Chl-*a*, the concentration gradients with depth were large in early spring (FEB), decreasing rapidly from high surface concentrations to a low background level within the top 3 cm (Fig. 4). During late spring (APR and MAY), the Chl-*a* gradients were still large, but the surface concentrations were lower and Chl-*a* penetrated deeper (about 5–6 cm depth). During summer (AUG) and fall (OCT/NOV), the surface concentrations of Chl-*a* at each site were remarkably lower and depth profiles showed more scatter or even a sub-surface maximum at a few cms depth. For phaeophorbide-*a* (Fig. 5) and pyropheophorbide-*a* (Fig. 6), the profiles followed basically similar patterns to Chl-*a* while phaeophytin-*a* (Fig. 7) often exhibited slightly increased concentrations. One difference between Chl-*a* and phaeopigment profiles was that the higher concentration gradients of phaeopigments often occurred during late spring, in contrast to the early spring maxima for Chl-*a* (Fig. 4). The ratios of individual phaeopigments to Chl-*a* exhibited different patterns, reflecting differences in the inputs of individual chloropigments and *in situ* degradation processes. For example, phaeophorbide-*a*/Chl-*a* ratios kept almost constant with depth while phaeophytin-*a*/Chl-*a* ratios often increased with depth (Fig. 8).

Inventories of Chl-*a* and phaeopigments can be obtained by integrating concentrations over the top 10 cm of sediments. Reactive inventory is defined here as the degradable fraction of pigment, the total inventory minus the lower, constant background inventory found below ~4–6 cm depth. Chl-*a* spatial inventory patterns in the Sound are represented by Figure 9 while phaeopigment spatial inventory

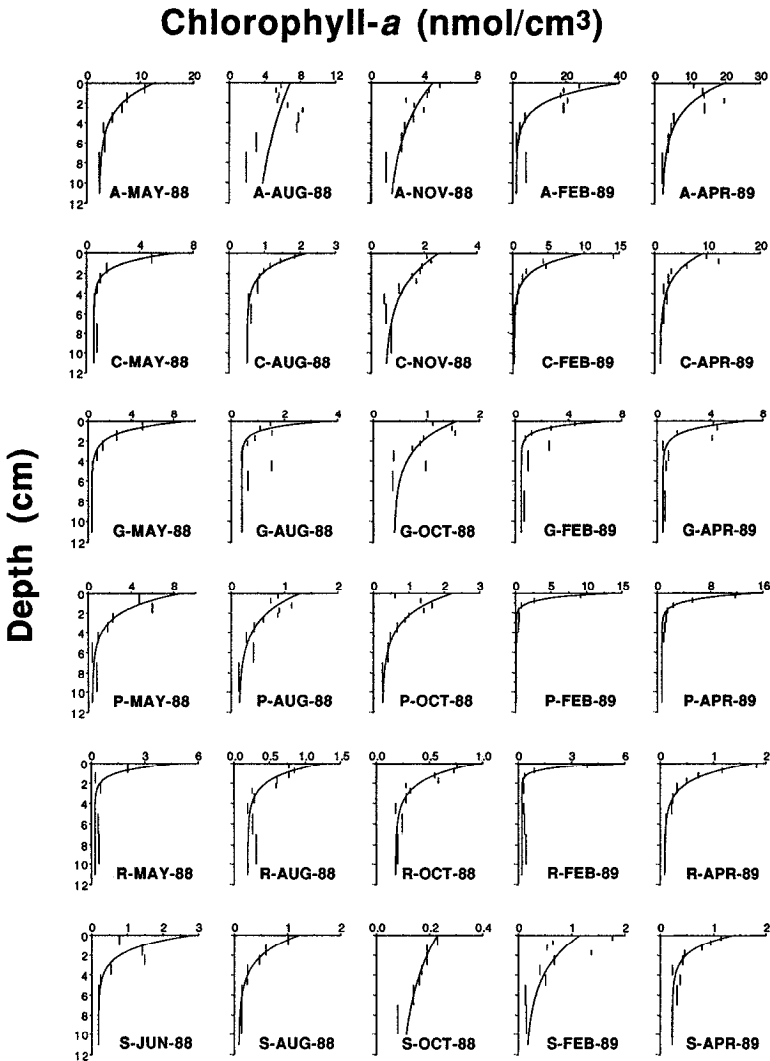


Figure 4. Seasonal depth profiles of Chl-*a* at 6 reference stations. Curves represent transport-reaction model fits to distributions.

patterns are represented by Figure 10. The seasonal reactive Chl-*a* inventories and total reactive phaeopigment inventories at 6 reference stations between MAY 88 and APR 89 are compared in Figure 11. These patterns demonstrate the similarity over similar spatial and seasonal scales between chloropigment surface concentrations and inventories integrated over the top 0–10 cm. Spatially, the highest inventories of both Chl-*a* and major phaeopigments were found in the western Sound where levels at least 2–10× those in the deep central Sound and the eastern Sound occurred at all

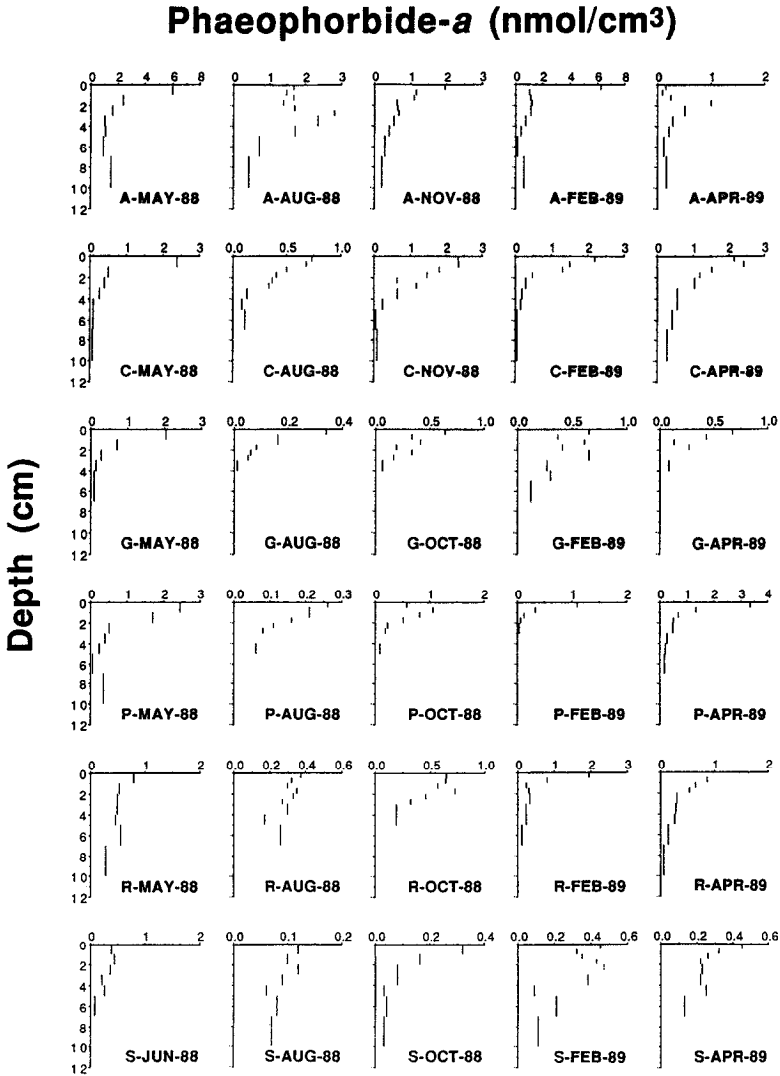


Figure 5. Seasonal depth profiles of phaeophorbide-a at 6 reference stations.

times of the year; intermediate levels often occurred along the north and south shores of the Sound. Seasonally, Chl-a inventories were greatest following the spring bloom and smallest during late summer and fall while phaeopigment inventories exhibited more irregular variations. The largest relative seasonal excursions in Chl-a inventories were found in the muddy, shallow (< 25 m) central Sound. During spring (high primary production due to bloom), sedimentary Chl-a reactive inventories seem to be water column depth-dependent: higher values in shallow areas and lower in deep areas (Fig. 12a).

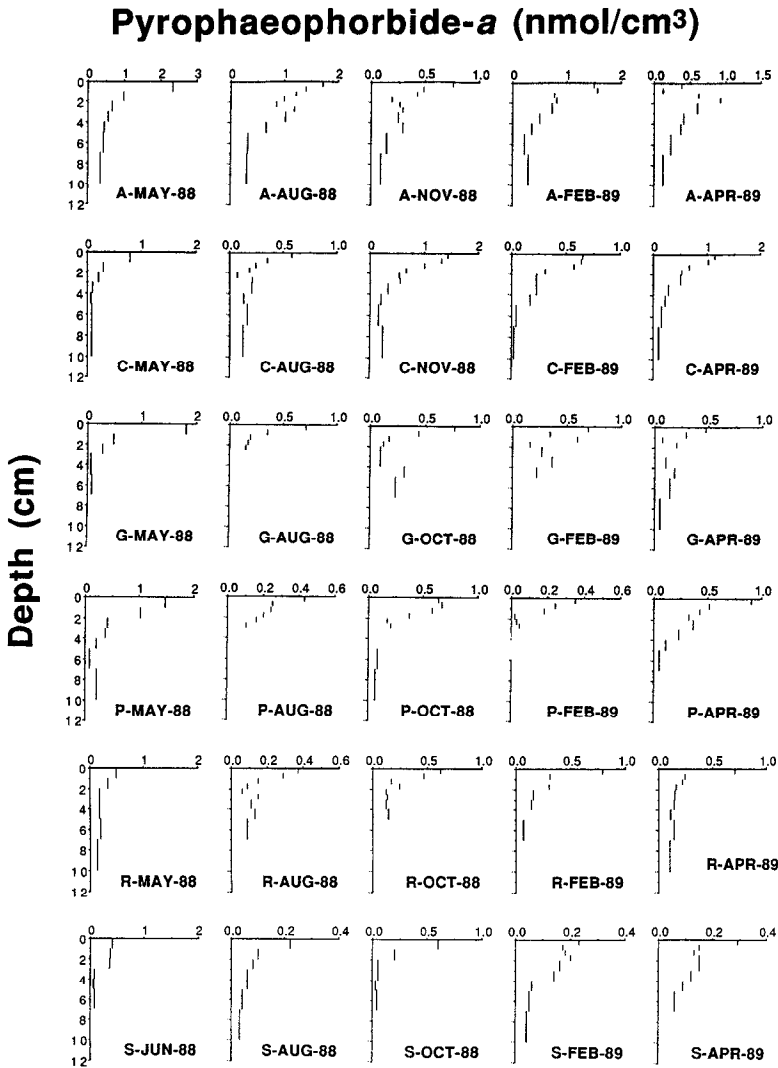


Figure 6. Seasonal depth profiles of pyrophaeophorbide-*a* at 6 reference stations.

4. Modeling and results

Previous work on the rates and mechanisms of Chl-*a* degradation in sediments has demonstrated that decomposition is primarily a pseudo first-order process (Sun *et al.*, 1993a). Decomposition rate constants for Chl-*a* in the present study can be estimated in two ways: by extrapolation of laboratory rates to *in situ* temperatures and by calculation from diagenetic models of concentration depth profiles. Extrapolations of laboratory rates in this case were based on incubations of intertidal Long Island Sound sediments (Flax Pond) under oxic conditions (Sun *et al.*, 1993a). Oxic

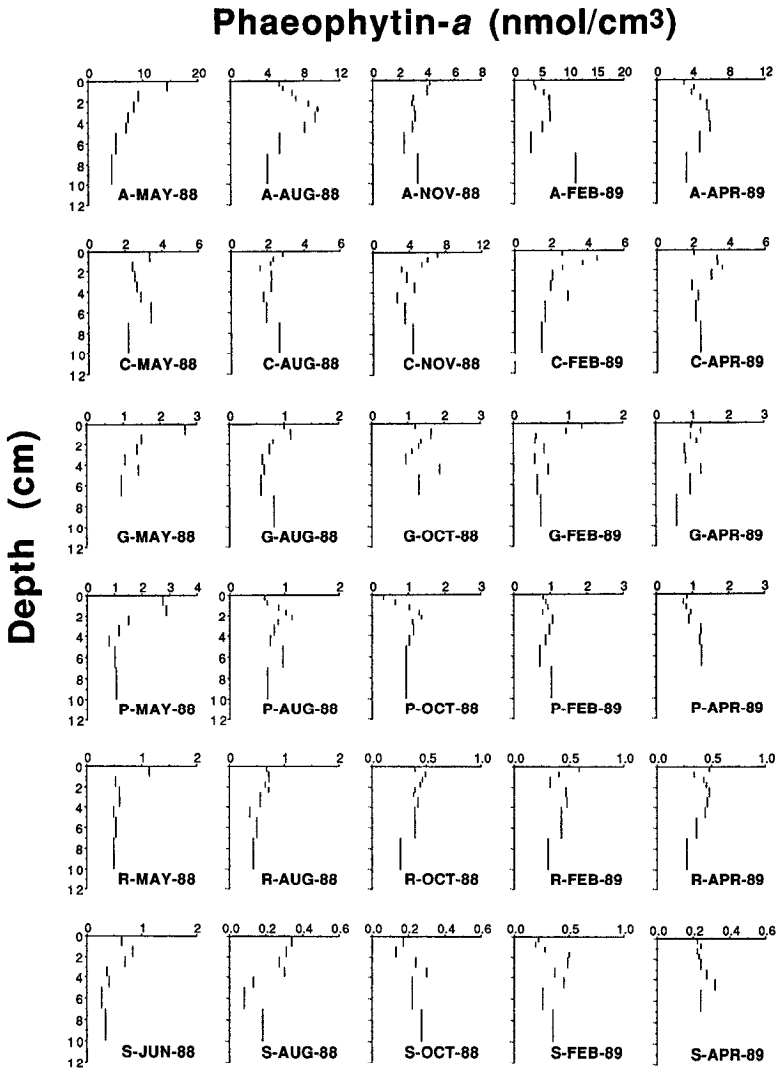


Figure 7. Seasonal depth profiles of phaeophytin-*a* at 6 reference stations.

rather than anoxic decomposition rate constants were used because comparisons of laboratory incubations with natural profiles of Chl-*a* suggest that sedimentary Chl-*a* degrades almost completely. Experiments demonstrate that nearly complete degradation requires either oxic conditions or functionally oxic conditions because of oscillating redox properties caused by bioturbation (Sun *et al.*, 1993a).

The decomposition rate constants estimated from laboratory incubation data (extrapolated to temperature of sample collection based on the equation $\ln k = 18.34 - 6160T^{-1}$, Sun *et al.*, 1993a) are compared in Table 3 to those calculated at the same sites from transport-reaction modeling of Chl-*a* profiles. The

Ratios of phaeophorbide-*a* and phaeophytin-*a* to Chl-*a*

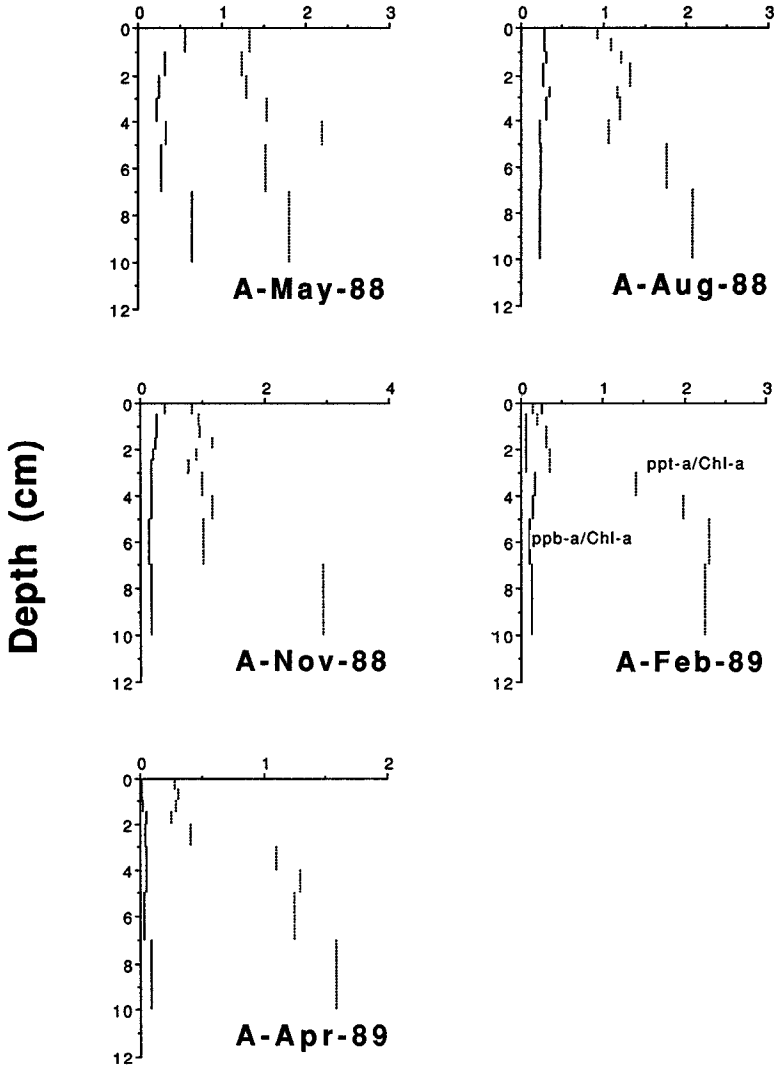


Figure 8. Seasonal variations of two ratios (phaeophorbide-*a*/Chl-*a*, solid lines; phaeophytin-*a*/Chl-*a*, dotted lines) with depth at station A.

model used is:

$$\partial C / \partial t = 0 = D_B (\partial^2 C / \partial z^2) - kC \tag{1a}$$

$$z = 0; c = C_T \text{ (constant)} \tag{1b}$$

$$z = \text{large}; C = C_B \tag{1c}$$

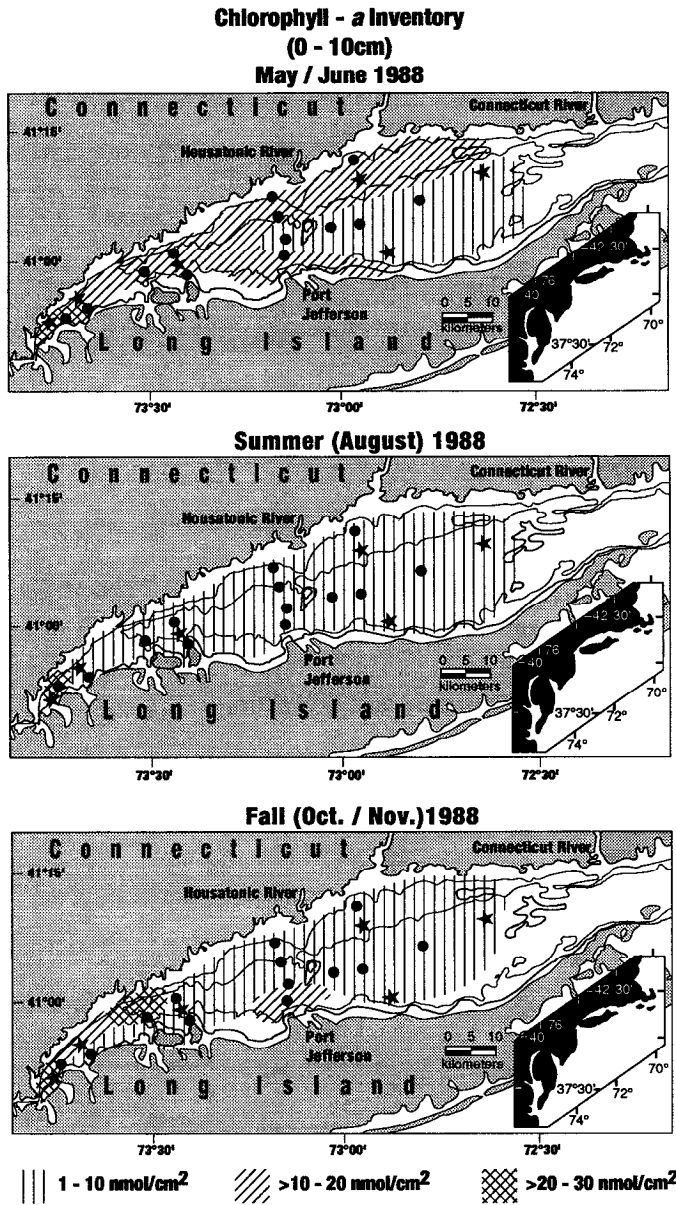


Figure 9. Chl-a inventory pattern (0-10 cm) during MAY/JUN, AUG, and OCT/NOV 1988.

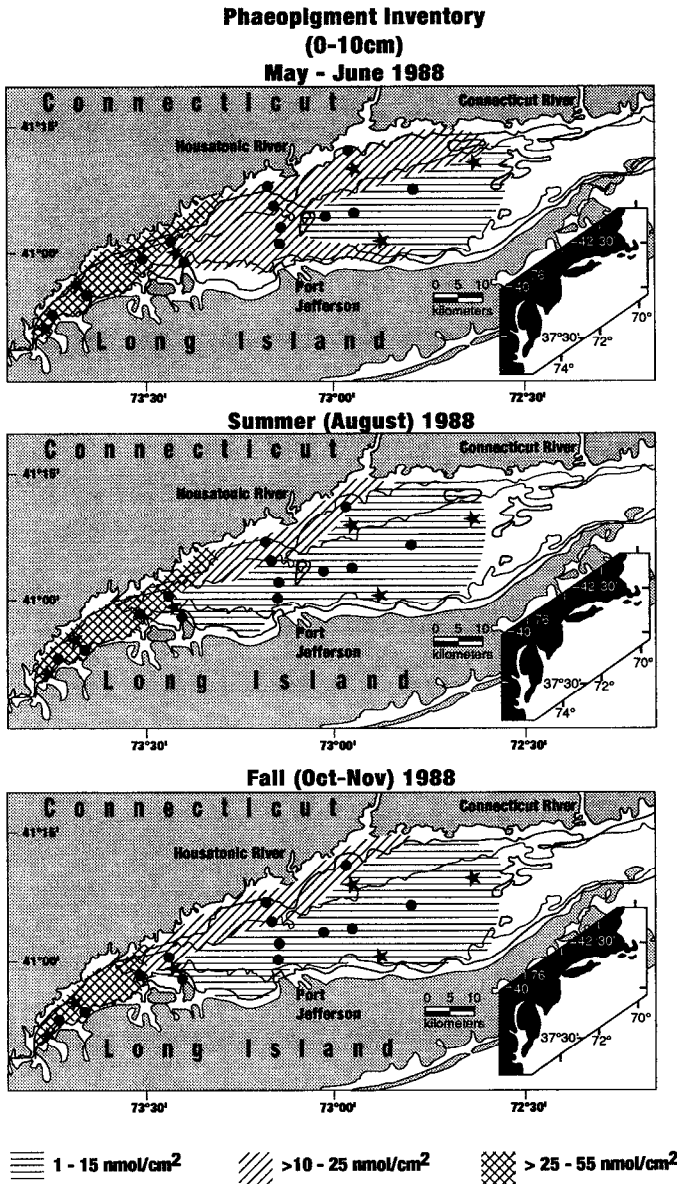


Figure 10. Phaeopigment inventory pattern (0–10 cm) during MAY/JUN, AUG, and OCT/NOV 1988.

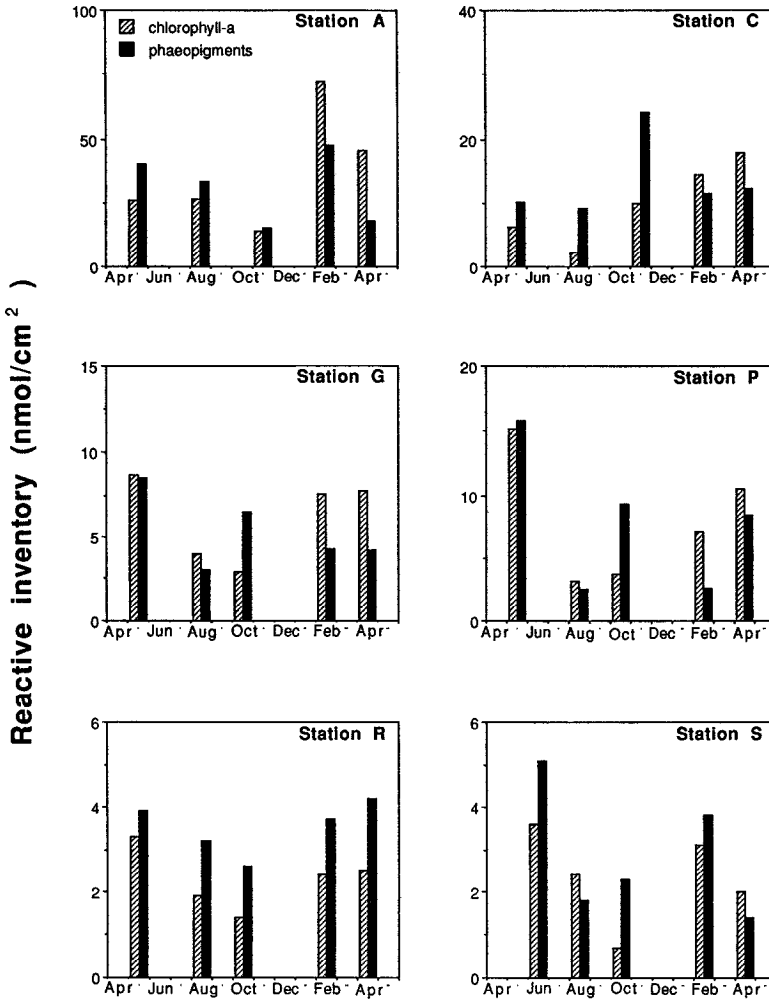


Figure 11. Comparison of seasonal inventories of Chl-a (cross-hatched) and total phaeopigments (stippled) at reference stations.

Giving:

$$C(z) = C_T \exp(-\sqrt{k/D_B}z) + C_B \tag{2}$$

Where:

z = depth, 0 at interface, positive into sediment

t = time

C_T = reactive concentration at the interface

C_B = background concentration

D_B = particle diffusive mixing coefficient

k = first order decomposition rate constant

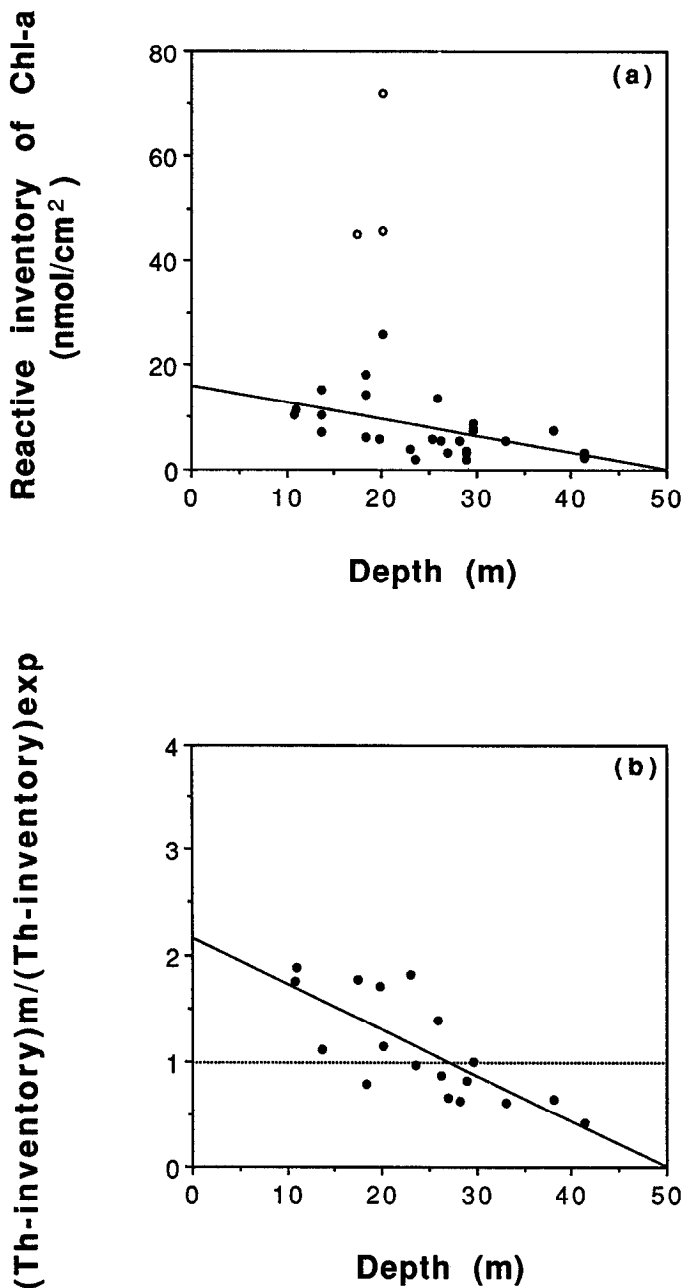


Figure 12. (a) Variations of Chl-a reactive inventory during spring with water depth. Regression line ($r^2 = 0.265$) was calculated based on closed circles; open circles represent extremely high values at the western station A; (b) Correlation between the ratio of measured excess ²³⁴Th inventory to expected ²³⁴Th inventory and water depth. Measured annual averaged excess ²³⁴Th inventories are calculated from data in Cochran and Hirschberg (1991) and agree generally with those of Aller *et al.* (1980). Dotted line is the ideal case if measured values are equivalent to expected values. Solid line is the correlation ($r^2 = 0.562$).

Table 3. Comparison of mean apparent first-order Chl-*a* decomposition rate constants (d^{-1}) derived from modeling Chl-*a* profiles using D_B from ^{234}Th distributions and calculated based on temperature-dependent oxic degradation.

	May	Aug	Nov	Feb	Apr
k_d (modeled)	0.074	0.146	0.065	0.550	0.327
k_d (calculated)	0.035	0.077	0.042	0.018	0.025

This simple model assumes local steady state (allowed by rapid decomposition). It also assumes constant D_B and k values in the top 0–4 cm of sediments and ignores sedimentation processes relative to mixing processes. The application and limits of the model with respect to Chl-*a* are discussed in detail by Sun *et al.* (1991). The model fits for Chl-*a* data are represented by curves in Figure 4. In the present cases, we used values of mixing coefficients, D_B , derived independently from vertical distributions of ^{234}Th in the same cores (Cochran and Hirschberg, 1991). The values of k necessary to fit Chl-*a* depth profiles given the D_B from ^{234}Th are compared to those extrapolated from laboratory incubations in Table 3. These comparisons demonstrate general agreement ($\sim 2\times$) between the two methods for most stations between MAY and NOV. Large differences occur between the estimates in the spring periods (FEB and APR), probably due to pulsed inputs of Chl-*a* caused by the annual phytoplankton bloom resulting in a highly non-steady state boundary condition relative to decomposition rates, contrary to assumptions. Mixing mechanisms may also change. In general, however, for much of the year agreement is good ($\sim 2\times$) and k values lie in the range of 0.02–0.15 d^{-1} (excluding FEB, APR).

The profiles for phaeophorbide-*a* (Fig. 5) suggest that first-order decomposition may also govern its distribution. To allow comparison with the experimental incubation rates for Chl-*a*, we calculated the rate constants for phaeophorbide-*a* relative to the assumed values for Chl-*a* in the same core at the reference stations (i.e., the ratio of the attenuation constants for exponential fits to the two pigment concentration depth profiles given by Eq. 2, and assuming identical D_B). The resulting values range from 0.017–0.286 d^{-1} , and appear to be ~ 2 – $3\times$ larger than that of Chl-*a* (Table 4).

Table 4. Apparent first-order decomposition rate constants (d^{-1}) of phaeophorbide-*a* in 6 reference station sediments. Calculation was based on particle reworking coefficients (D_B) estimated from Chl-*a* distributions, coupled with decomposition experiments.

Station	May/June	Aug	Oct/Nov	Feb	Apr	Mean
A	0.138	0.044	0.822	0.011	0.079	0.218
C	0.020	0.026	0.278	0.018	0.037	0.076
G	0.046	0.119	0.140	0.003	0.091	0.080
P	0.039	0.181	0.171	0.011	0.008	0.084
R	0.007	0.043	0.020	0.004	0.012	0.017
S	0.010	0.041	0.807	0.006	0.032	0.179
Mean	0.043	0.076	0.373	0.009	0.043	0.109

The apparent decomposition rate constant of phaeophorbide-*a* in other sediments, for example, Dabob Bay, Washington, U.S.A., is $\sim 0.017 \text{ d}^{-1}$ (Furlong and Carpenter, 1988) and within the range calculated here.

5. Discussion

a. Spatial patterns. Sedimentary chloropigments in LIS may derive from primary production in surface waters, benthic regions of the euphotic zone, or the terrestrial drainage area. Local benthic production is minimal at the sample sites which, due to high turbidity during most times of the year, normally lie below the euphotic zone. A variety of diagenetic studies of decomposition stoichiometry indicate that dynamic pools of sedimentary organic matter in LIS are predominantly of marine origin (e.g., Krom and Berner, 1981). Thus, direct terrestrial sources are unlikely to strongly influence labile compounds such as Chl-*a* in the basin as a whole. Water column production in immediately overlying water and lateral redistribution of material within the estuary must therefore represent the major potential sources of reactive pigments at a given subtidal site.

Water column phytoplankton biomass and productivity are higher in western than in central LIS (Riley and Conover, 1956; Stacey, recent unpublished data) due to higher nutrient loading from human population centers and benthic nutrient regeneration in the relatively shallow western region (Bowman, 1977; Wolfe *et al.*, 1991; Aller and Benninger, 1981). The spatial patterns of surface sedimentary chloropigment concentrations (Fig. 3) generally correspond to the patterns of overlying water column Chl-*a* and productivity. Primary production in the immediately overlying surface waters therefore seems to be a major factor controlling the delivery of reactive organic matter to sediments in much of subtidal LIS. Because of the shape of the Sound, the east to west increase in sedimentary pigments could also reflect progressively greater influence of inputs from coastal boundary benthic production.

Factors that redistribute particles laterally may alter any simple correlation of water column or coastal boundary sources with sediment reservoir composition. For example, although primary production in central LIS is probably relatively spatially uniform on the average, substantial variation in sediment inventories of chloropigments occur within the central basin. The distribution of the natural radionuclide ^{234}Th ($t_{1/2} = 24 \text{ d}$) in LIS sediments gives insight into the likely influence of lateral transport processes on chloropigment inventories. Correlation between the ratios of ^{234}Th inventories measured by Cochran and Hirschberg (1991) in the same cores used for Chl-*a* sampling in the present study and “expected” ^{234}Th inventories based on overlying water depth (Fig. 12b), demonstrates that more ^{234}Th (measured $>$ expected values from immediately overlying ^{238}U source) is deposited in shallow stations than in deep stations despite a greater potential water column source over deeper sites (see also, Aller *et al.*, 1980). There is negligible dissolved ^{234}Th in LIS so any increased solute scavenging over shallow regions has little effect

on inventory patterns. Chl-*a* inventory patterns apparently indicate a similar tendency for capture of reactive components by particle exchange in shallow regions, at least during the spring when relatively high primary production occurs (Fig. 12a).

b. Seasonal variation. Temporal variations of sedimentary chloropigments in LIS mirror the overall seasonal variations of phytoplankton production in the water column. Higher surface concentrations (upper 1 cm) and inventories in the upper 10 cm occur in spring, immediately after the major annual bloom, while lower values occur in summer and fall (Figs. 3 and 11). However, there seems to be a time lag between maximum values for Chl-*a* in early spring and those for total identified phaeopigment in late spring. This offset in maximum concentrations may reflect reactions occurring both in the water column and at the seafloor.

Chl-*a* in intact cells can be converted into phaeopigments during grazing by zooplankton (Shuman and Lorenzen, 1975; Downs, 1989). The lag between the appearances of Chl-*a* and the phaeopigments in sediments may reflect the difference in time-dependent growth patterns of water column phytoplankton and the later delivery of zooplankton feces to the bottom. In LIS, the offset between maximum primary production in late winter-early spring (Conover, 1956) and maximum zooplankton abundance (and hence grazing) in APR and MAY (Peterson, 1986) is similar to the lag between maximum sedimentary Chl-*a* and phaeopigment inventories. The differential rates of pigment conversion in bottom sediments should also produce the observed relative inventory successions (Sun *et al.*, 1993a) but, as shown subsequently, vertical profiles imply a more substantial role for water column or surface-most sediment reactions.

Surface concentrations of chloropigments exhibit relatively stronger seasonal changes than the inventories (Figs. 3 and 11) because inventories reflect input and degradation processes integrated over longer time scales. Rudnick and Oviatt (1986) demonstrated that time lags on the order of months can exist between maximum deposition and maximum benthic mineralization of phytoplankton detritus. The spring bloom can provide very high deposition of organic carbon; however, minimal metabolic processes due to low temperature at the time of deposition may cause temporary storage of labile organic matter in sediment. Mixing processes due to bioturbation can also transport labile organic matter from the interface to deeper sediments, decreasing surface concentrations. With the increase of temperature in summer, mineralization of organic carbon and mixing speed up due to increased benthic organism activity.

c. Depth penetration patterns. Depth distributions of chloropigments are mainly controlled by mixing and degradation processes. The nearly exponential decrease of Chl-*a* with depth in many cases (Fig. 4) demonstrates that degradation is faster than particle transport. Characteristic penetration to background level is ~4–5 cm. The

depth profiles of phaeophorbide-*a* and pyropheophorbide-*a* (Fig. 5 and 6) exhibit a trend similar to Chl-*a*, implying that the source of these two phaeopigments is predominantly from the overlying water or the surface-most layer of sediment. In contrast, the profiles of phaeophytin-*a* (Fig. 7) often exhibit a slight increase with depth, although there is a decreasing trend in late spring when zooplankton grazing and presumably delivery from the water column is highest (Peterson, 1986).

The increase in phaeophytin-*a* concentration with depth implies significant *in situ* production due to Chl-*a* degradation within sediments. Experiments using ¹⁴C-labelled Chl-*a* and phaeophytin-*a* reveal that phaeophytin-*a* is one of the major products of Chl-*a* degradation in LIS sediments and can be preserved for at least one month under anoxic conditions (Sun *et al.*, 1993b). Comparisons of phaeophorbide-*a*/Chl-*a* and phaeophytin-*a*/Chl-*a* ratios with depth (Fig. 8), further indicate differences in the diagenesis of these two phaeopigments. The ratios of phaeophorbide-*a*/Chl-*a* are often constant or decrease slightly with depth, implying that phaeophorbide-*a* may decay at a similar or faster rate compared to Chl-*a*. On the other hand, the ratios of phaeophytin-*a*/Chl-*a* always increase with depth, suggesting that either phaeophytin-*a* accumulates due to production during Chl-*a* degradation or decays at a lower rate than Chl-*a*.

In general, relatively larger concentration gradients occur with depth and reactive chloropigments penetrate only 2–4 cm during spring when deposition of chloropigments from the overlying water is high. Smaller concentration gradients are present during summer and fall and subsurface maxima can sometimes occur. Reactive chloropigments penetrate deeper (4–8 cm) at this time although supply is presumably lower. Subsurface maxima in pigment profiles may be caused by several processes: variable input, vertical and lateral transport (²³⁴Th analog), and variable decay rates and mechanisms with depth. Vertical transport within deposits involves both diffusive mixing (dependent on concentration gradient) and nondiffusive (advective) mixing. Diffusive mixing together with depth-independent decay cannot result in subsurface maxima, even with variable input. When surface input is low and activities of organisms become more intense during warmer periods, nondiffusive mixing may dominate vertical transport of pigments through ‘conveyor-belt’ feeding (e.g., Boudreau, 1986; Rice, 1986; Robbins, 1986).

Bioturbation also leads to oscillation of particles between oxic and anoxic conditions during mixing and resuspension (Aller, 1982). Different degradation pathways of pigments under oxic and anoxic conditions may cause a degree of depth-dependent decomposition when redox zonations are present in the sediments. However, because these redox zonations are transitory, it seems likely that some combination of non-diffusive mixing and depth-dependent reaction is required to explain subsurface maxima.

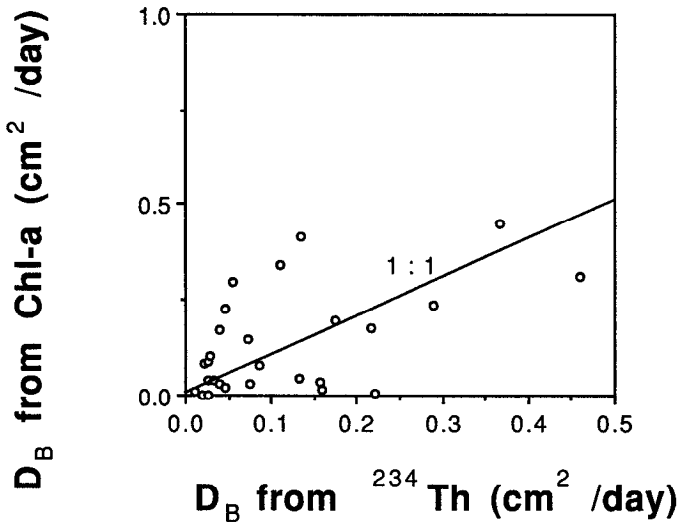


Figure 13. Comparison between particle reworking coefficients derived from Chl-*a* distributions and those derived from ^{234}Th distributions at 6 reference stations.

d. Particle reworking and benthic organism activities. Particle reworking coefficients (D_B) for LIS sediments can be estimated using Chl-*a* as a tracer (Sun *et al.*, 1991). The basic method is to use a steady-state model of depth distributions of Chl-*a* that is based on temperature-dependent decomposition rate constants extrapolated from laboratory experiments (e.g., $k = 0.017 - 0.079 \text{ d}^{-1}$ when $T = 2 - 22^\circ\text{C}$). Using model equations 1–2, we calculated the value of D_B necessary to fit Chl-*a* profiles using experimental values of k at the appropriate temperature of collection. The comparison (Fig. 13) between particle reworking coefficients derived either from Chl-*a* or from ^{234}Th distributions at the 6 reference stations shows a general correlation between these two estimates seasonally. This method of evaluating the consistency between behavior of the two tracers, the validity of the transport-reaction model, and the overall decomposition kinetics of Chl-*a* is an alternative to comparing rate constants as done in Table 3.

The mean particle reworking coefficients (D_B) for the entire LIS, western LIS, and central LIS calculated using Chl-*a* profiles at all stations are also roughly comparable with those estimated from ^{234}Th distributions (Table 5). Particle reworking coefficients obtained from these two independent tracers show that higher mixing occurs in late summer/early fall when water temperature is highest and relatively lower mixing occurs during colder periods (spring). However, D_B values estimated from Chl-*a* distributions exhibit a distinctly stronger seasonal variation than those from ^{234}Th distributions, that is, higher values during summer/fall but even lower values during early spring (higher amplitude of oscillation).

Table 5. Comparison of mean particle reworking coefficients (D_B , cm^2/d) derived from Chl-*a* and ^{234}Th distributions.

Whole LIS (19 stations)					
	May	Aug	Oct	Feb	Apr
D_B - ^{234}Th	0.068	0.142	0.103	0.110	0.099
D_B -Chl- <i>a</i>	0.137	0.398	0.334	0.041	0.047
Western LIS (Sta. A, B, C, D, E, F, G, and H)					
D_B - ^{234}Th	0.106	0.152	0.138	0.108	0.135
D_B -Chl- <i>a</i>	0.118	0.477	0.372	0.020	0.068
Central LIS (Sta. I, J, K, M, N, P, Q, R, S, U, and W)					
D_B - ^{234}Th	0.046	0.133	0.084	0.113	0.063
D_B -Chl- <i>a</i>	0.150	0.330	0.309	0.062	0.026

There are several possible explanations for differences between D_B estimated from Chl-*a* fluxes and that from ^{234}Th fluxes. First, as discussed in Sun *et al.* (1991), the simple assumption of 'local' steady state can result in substantial uncertainties in calculations of J (flux) and D_B . Fluxes of ^{234}Th are presumably seasonally closer to steady state than those of Chl-*a*, which are realistically more periodic or pulsed inputs. Second, different mixing processes by macrofauna and meiofauna due to the differences in feeding type, life habit, mobility, and food quality as well as fresh content may cause selective mixing of organic particles containing Chl-*a* pigment relative to bulk sediments (see also, Smith *et al.*, 1993). Third, physical mixing by waves and currents, combined with occurrence of hypoxia, may influence Chl-*a* and ^{234}Th reworking processes differently. Fourth, as implied earlier, extrapolation of laboratory derived rate constants to the field may be at least partially suspect. Nevertheless, the overall agreement is quite good, indicating that Chl-*a* represents an alternative to radioisotopes in the quantification of sediment mixing processes in LIS.

e. Estimation of planktonic carbon flux. The flux of particulate organic matter to sediments fuels the benthic communities and through its degradation influences the geochemical cycles of many elements. Unlike the open ocean, there are several major labile organic carbon sources in addition to primary production (e.g., river input, runoff, and sewage loading) in estuaries such as LIS. Differentiating between these sources is difficult; however, estimates can be made of likely marine carbon inputs from the Chl-*a* inventories by assuming a phytoplankton origin for Chl-*a*. In LIS, the weight ratios of phytoplankton C:Chl-*a* were 58 ± 7.7 in surface water and 68 ± 6.5 in bottom water over a one year period (Tantichodok, 1989). In principle, if the fluxes of Chl-*a* into sediments are known, then the corresponding phytoplanktonic carbon flux, J_{org} , can be calculated by using an appropriate ratio of phytoplankton C:Chl-*a*.

Table 6. Comparison of mean planktonic carbon fluxes (mmol/m²/d) derived from Chl-*a* inventories and mean organic carbon fluxes (mmol/m²/d) derived from O₂ uptake rates.

	Whole LIS (19 stations)					
	May	Aug	Oct	Feb	Apr	Annual mean
$J_{\text{org}} \sim \text{O}_2 \text{ uptake}$	22.7	11.1	14.7	6.93	16.8	~ 14.4
$J_{\text{org}} \sim \text{Chl-}a$	16.1	14.6	7.95	15.9	16.5	~ 14.2
	Western LIS (Sta. A, B, C, D, E, F, G, and H)					
$J_{\text{org}} \sim \text{O}_2 \text{ uptake}$	29.2	10.4	15.9	8.43	17.0	~ 16.2
$J_{\text{org}} \sim \text{Chl-}a$	24.2	21.3	13.0	28.4	27.4	~ 22.9
	Central LIS (Sta. I, J, K, M, N, P, Q, R, S, U, and W)					
$J_{\text{org}} \sim \text{O}_2 \text{ uptake}$	17.4	11.5	14.0	5.43	16.6	~ 13.0
$J_{\text{org}} \sim \text{Chl-}a$	10.2	9.37	4.97	3.25	5.48	~ 6.7

Assuming overall first-order decomposition kinetics, we can estimate the seasonal fluxes of Chl-*a* into the sediments simply by multiplying inventories by the corresponding decomposition rate constants (assuming local steady state). We have done this for the LIS stations using the measured reactive Chl-*a* inventories and laboratory measured rate constants corrected for temperature at time of collection. Calculation of the corresponding phytoplankton carbon flux (taking an averaged weight ratio of phytoplanktonic C:Chl-*a* as 60:1) implies that carbon fluxes to the sea floor range from 1 to 90 mmol/m²/d¹. Fluxes in the far western Sound (Stations A, B, C, and D) are 2–10× those of the central LIS region. The annual mean phytoplankton carbon flux calculated for LIS by this method is 14 mmol/m²/d¹ (Table 6). This value suggests that about 30% of phytoplankton carbon produced by photosynthesis in LIS may be delivered to the sea floor based on Riley's (1956) estimate of primary production.

An alternative estimate of reactive organic carbon flux is based on the oxygen flux across the sediment-water interface and can be compared to that predicted by the simple model of Chl-*a* decomposition and supply described above. According to the Redfield ratio for phytoplankton organic matter, about 77% of the oxygen consumed in the decomposition of organic matter will be used to oxidize organic carbon to CO₂ (initial average C oxidation state = 0). Thus, if we assume that all the oxygen diffusing across the sediment-water interface is consumed by the degradation of organic matter (including complete oxidation of anaerobic metabolites such as S), then the flux of O₂ across the sediment-water interface can be converted into the flux of labile organic carbon using the ratio 0.77. Carbon fluxes derived in this way from the measured O₂ fluxes to bottom sediments (Mackin *et al.*, 1991) show general agreement (about a factor of 2) with those estimated from Chl-*a* fluxes at most stations during periods when the water column is well-oxygenated (Table 6).

Large deviations between the two methods occur in western LIS. For example, at Station A, the ratio of J_{org} estimated from the Chl-*a* method to the J_{org} estimated from

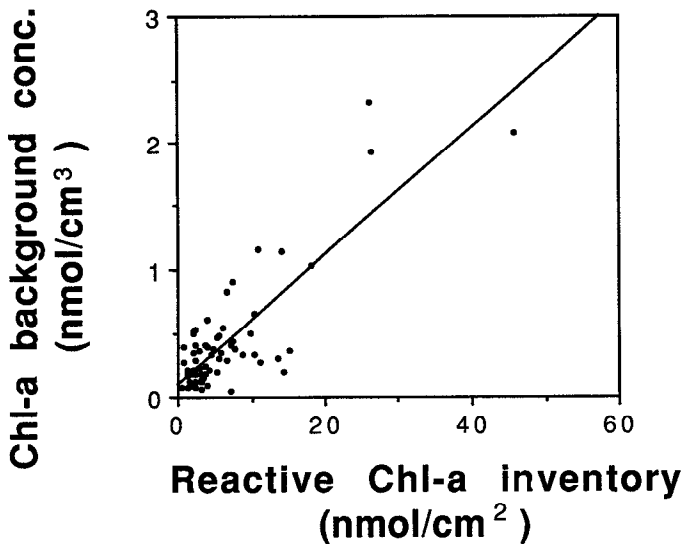


Figure 14. Correlation between Chl-*a* background concentration and Chl-*a* reactive inventory in all LIS stations ($r^2 = 0.678$).

the O_2 method was $\gg 1$. The most likely reasons for these deviations are water column hypoxia caused by decomposition of labile organic matter in both water column and sediments (oxygen limited diffusive fluxes), and storage of anaerobic products in the deposits. Estimates of carbon flux from oxygen flux are biased by seasonal imbalances between aerobic and anaerobic metabolism (e.g., Sampou and Oviatt, 1991) but annual averages should reflect delivery unless storage of anaerobic products such as S is high. The direct contribution of O_2 to total organic matter decomposition in estuarine sediments like LIS is relatively small ($< 20\%$, Mackin and Swider, 1989), and most of the O_2 flux represents reoxidation of anaerobic metabolites. The most labile components of organic matter are believed to originate from marine sources but non-planktonic carbon from river inputs, runoff, and sewage (bacterial carbon) loading also consumes O_2 . On the other hand, the use of a constant phytoplankton C:Chl-*a* ratio in the technique using Chl-*a* to estimate phytoplankton carbon fluxes may lead to an underestimation due to degradation processes occurring in the water column. Chl-*a* estimated fluxes are also higher during the spring bloom period generally (Table 6), perhaps reflecting temporary C storage due to low temperature or shifts to net anaerobic metabolism during heavy loading. Again, however, models of Chl-*a* decomposition provide an apparently valid estimate of C flux to the bottom in estuarine environments where other methods are often fraught with larger errors.

Background Chl-*a* concentrations below 5 cm also show a spatial pattern similar to pigment inventory distributions: higher values occur in western than central LIS

(Table 2). The correlation between Chl-*a* background concentration and reactive inventory (Fig. 14) is likely due to the influence of supply rate of organic matter. Higher supply rates result in higher sediment reactive inventories and higher background concentrations of Chl-*a*. The higher background may reflect a tendency to preserve a relatively constant proportion of the C flux. It may also be due to lack of efficient reoxidation in high flux areas because of lower bioturbation associated with water column oxygen depletion. The concentration of organic matter in the mixed layer is directly proportional to the particulate flux to the sediments (Berner, 1980); this relationship can be modified by transport processes and oxidant availability but the direct relationship between carbon content of the sediments and particulate flux is not altered (Emerson and Hedges, 1988). Thus, for a variety of reasons, both the Chl-*a* background concentration and the reactive inventory will be high when supply is high, and low when supply is low.

5. Conclusions

The surface (0–1 cm) concentrations and inventories (0–10 cm) of sedimentary chloropigments vary spatially and temporally in Long Island Sound sediments. Higher values (2–10×) occur in western LIS than in central LIS, corresponding to similar historical patterns of phytoplankton biomass distributions in the water column. This close relationship between sedimentary chloropigments and historical biomass data in the water column suggests that primary production in immediately overlying surface water is a dominant factor controlling supply to the sea floor. In addition to direct supply of pigments, both lateral transport and water depth may also be important factors affecting redistribution of pigments in LIS sediments. Seasonal changes in sedimentary chloropigments basically follow the primary production pattern in surface water: maximum values occur in spring and minima in summer and fall. However, the time lag between maximum Chl-*a* and phaeopigment inventories may be related to the effects of time-dependent grazing of zooplankton in the water column and temperature-dependent metabolic processes in the sediments.

The vertical distributions of chloropigments with depth demonstrate that decomposition processes are faster than mixing processes. In general, Chl-*a* profiles exhibit an exponential decrease with depth. Irregular profiles (subsurface maxima) occurring during warmer times may be caused by seasonally variable inputs, temperature-dependent activities and nondiffusive mixing by benthic organisms, and redox zonation in the surface sediments. Profiles of phaeophorbide-*a* and pyropheophorbide-*a* follow the same basic pattern as Chl-*a* but the ratios of phaeophorbide-*a*/Chl-*a* often decrease with depth, implying that no net production of phaeophorbide-*a* occurs, or that it decays relatively faster than Chl-*a*. In contrast, the concentrations of phaeophytin-*a* often increase slightly or are constant with depth while the ratios of phaeophytin-*a*/Chl-*a* always increase with depth, suggesting that

production of phaeophytin-*a* in LIS sediments is due to the degradation of Chl-*a* and that phaeophytin-*a* may be relatively well preserved.

Using temperature-dependent first-order decomposition rate constants obtained from related anoxic-oxic decomposition experiments, Chl-*a* fluxes were estimated from sedimentary Chl-*a* inventories. Planktonic carbon fluxes can be estimated from conversion of Chl-*a* fluxes by using average planktonic carbon/Chl-*a* ratios (60:1) observed in LIS plankton. These fluxes are comparable (within a factor of 2) to carbon fluxes estimated from O₂ fluxes across the sediment-water interface. Initial estimates of sediment particle mixing coefficients, D_B , from the Chl-*a* distributions presented here are roughly comparable with those estimated from ²³⁴Th distributions in the same sediments. Magnitudes of D_B estimated using the two tracers are generally within a factor of 2–5×. Seasonal patterns of D_B from the two independent tracers are also similar: higher values occur during summer than during colder periods. Differences in D_B values estimated using the two tracers (Chl-*a* and ²³⁴Th) may be related to assumptions regarding boundary conditions (fluxes), style of mixing (diffusive, advective), and depth-independent reaction rates in the case of ²³⁴Th. Nevertheless, given these assumptions and accumulated errors in measurements, the agreement between the two tracers is remarkable.

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