

Aphotic Pigment Degradation in the Hypolimnion: Implications for Sedimentation Studies and Paleolimnology



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Aphotic pigment degradation in the hypolimnion: Implications for sedimentation studies and paleolimnology

Abstract—Reversed-phase high pressure liquid chromatography was used to quantify carotenoid and Chl degradation resulting from bacterial and microfaunal action during aphotic, hypolimnetic incubations of natural phytoplankton assemblages and detrital material in three lakes. Decay of carotenoids (to -0.0870 d^{-1}) and chlorophylls (to -0.1226 d^{-1}) was potentially rapid but site-specific. Chl *a* decay spanned a wide range (to -0.1226 d^{-1}) with greatest losses in circumneutral, unstained Peter Lake and least in acidic, stained Tuesday Lake. The usefulness of Chl *a* as an indicator of algal sedimentation was compromised by its rapid degradation, lack of compensatory production of recognizable derivatives, and an abundance of unknown, chlorophyllous compounds. β -carotene degraded less rapidly and variably (to -0.0167 d^{-1}) and is a useful addition to both sedimentation and paleolimnological studies. Differences among ca-

rotenoids in decay pose difficulties in reconstructing accurate estimates of former algal community composition, especially dinoflagellates, whose peridinin decays rapidly (-0.0843 d^{-1}). Changes in the relative (within-core) abundance of individual pigments may be combined, however, with changes in Chl *a*: β -carotene ratios to differentiate between periods of enhanced productivity (or pigment preservation) and changes in the vertical zonation of algal communities.

Chlorophylls and carotenoids have been used to monitor algal standing crop dynamics (Ridout and Morris 1985; Foy 1987), sedimentation of autochthonous production (Welschmeyer and Lorenzen 1985a; Carpenter et al. 1988), and postglacial changes in productivity (Sanger 1988). Both pigment sedimentation rates and abundance in surface sediments are correlated with primary productivity (Gorham et al. 1974; Guilizzoni et al. 1983), but the relations are often weak and may reflect lake-specific variation in loss processes (Brenner

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and Binford 1988). Little is known of the kinetics or relative importance of degradative mechanisms in freshwaters. Pigment degradation resulting from bacterial or microfaunal action is particularly poorly documented.

Herbivore grazing and photo-oxidation interact in complex ways to regulate pigment flux from the photic zone (Welschmeyer and Lorenzen 1985*a,b*; Carpenter et al. 1986, 1988). Although grazing by small-bodied zooplankton rapidly degrades pigments (Carpenter and Bergquist 1985; Klein et al. 1986), large cladocerans and copepods produce feces that sink rapidly and bypass the photo-oxidation that would otherwise completely destroy detrital pigments within a few days (Carpenter et al. 1988). Although grazing by large herbivores also reduces absolute pigment abundance, pigment concentrations [$\text{nmol (g organic matter)}^{-1}$] may increase due to selective degradation of unpigmented material (Leavitt and Brown 1988).

Once removed from the photic zone, pigments may continue to degrade. In vitro studies show that the rate and extent of this microbially mediated pigment degradation is great but may be pigment- or alga-specific (Daley and Brown 1973; Cranwell 1976; Leavitt 1988). Quantification of bacterial decomposition of pigments in situ is rare. Comparisons of sediment-trap catch and mean pigment concentration in surface sediments suggest that pigment decay in deep waters is rapid under oxic conditions ($>1\% \text{ d}^{-1}$) (Furlong and Carpenter 1988; Hurley 1988). These estimates do not, however, partition losses among different sources of destruction (biotic or abiotic in water or sediments). Because sediment traps are usually suspended in hypolimnetic waters of lakes for 2 weeks or more (Bloesch and Burns 1980), pigment degradation in deep waters may bias sedimentation estimates and create difficulties in interpreting the paleolimnological record (cf. Binford et al. 1983; Swain 1985).

We report the use of reversed-phase high pressure liquid chromatography (RP-HPLC) to quantify carotenoid and Chl degradation during aphotic, hypolimnetic incubations of water containing natural phytoplankton as-

semblages and detrital particles in three northern Michigan lakes. Chl *a* and β -carotene, the two ubiquitous pigments in phytoplankton, were compared as potential indicators of total algal sedimentation. Differences in initial oxygen concentration allowed us to compare decay rates under oxic and anoxic conditions. The experimental design takes advantage of zooplankton distribution and the abiotic environment to assign pigment losses to bacterial and microfaunal sources.

Incubations of hypolimnetic water were conducted during 1986 and 1987 summer stratification in Peter, Paul, and Tuesday Lakes in northern Michigan (section 36, T45N, R42W, Gogebic Co., Michigan) (Table 1). Physical and chemical data (Table 1) and initial pelagic phytoplankton communities were determined following Carpenter et al. (1986, 1987, 1988). Because all three lakes have distinct algal communities near the base of the photic zone (2–7% incident light), epilimnetic and metalimnetic populations were counted separately. Phytoplankton counts from the 3 weeks before the start of each experiment were pooled to determine initial epilimnetic algal communities, whereas metalimnetic communities included only samples taken within 1 week of the start of each trial. This procedure accounted for the longer time required for epilimnetic plankton sedimentation and allowed estimation of the initial phytoplankton composition in deep, aphotic waters—otherwise impossible due to high detrital content. Direct bacterial counts were not attempted because of the high degree of particulate aggregation common in these traps.

In each lake and year, water was drawn from a deep Chl maximum with a Van Dorn sampler, pooled, and delivered to 1-liter bottles that admitted no light. Water was collected from aphotic regions ($<1\%$ incident light) below the depth of the dominant, migrating crustacean zooplankton ($<1 \text{ Daphnia liter}^{-1}$) (Dini and Carpenter 1988; Dini unpubl. data). Daphnid densities were $<4\%$ of those that can occur in these lakes (Dini and Carpenter 1988). Samples were incubated in aphotic waters of constant, similar temperature near the depth of col-

Table 1. Characteristics of study lakes and experimental conditions. Maximal depth— Z_m ; photic zone depth, defined as depth of penetration of 1% incident light— Z_c ; absorbance of filtered water (440 nm)— A_{440} (Elser 1987).

	Peter		Paul		Tuesday	
	1986	1987	1986	1987	1986	1987
Z_m (m)		19.6		15.0		19.0
Area (ha)		2.1		1.2		0.79
Z_c (m)		7.5		5.5	2.75	4.0
A_{440}		0.49		0.80		1.68
CD* (m)	8		10	8	8	8
ID† (m)	8		11	6.5	10	7
Temp (°C) at ID	5		4.9	4.9	5.2	4.3
[O ₂] (mg liter ⁻¹) at CD	4.9		0.2	0.8	0.1	1.05
pH at Z_c	6.3		6.6	5.6	6.3	5.4

* Collection depth.

† Incubation depth.

lection (Table 1). Replicate bottles were removed monthly in 1986 and weekly in 1987.

After incubation, samples were concentrated onto Whatman GF/F filters and stored in airtight containers at -20°C . Visual inspection of filters confirmed that large herbivores were rare (<1 *Daphnia* liter⁻¹). Pigments were extracted within 3 weeks of collection by soaking filters 24 h at 12°C in a mixture of acetone, methanol, and water (80:15:5 by vol). Extraction was nonselective and 95% complete in comparison with exhaustive extractions and sonication (Leavitt and Brown 1988). Extracts were filtered (0.2- μm Acropore membrane filter), dried under a stream of nitrogen gas, sealed, and stored at -20°C until analysis. No pigment degradation resulted from this procedure (Carpenter et al. 1986). Extractions were conducted under low, indirect lighting with degassed HPLC-grade solvents.

Carotenoid and Chl concentrations were quantified by RP-HPLC (modified from Mantoura and Llewellyn 1983) with a Beckman model 421 controller, model 110A pumps, and model 165 detector, a Rainin Microsorb C₁₈ column (5- μm particle size), and a Shimadzu electronic integrator. Pigment samples were dissolved in a mixture of acetone, ion-pairing reagent (IPR), and methanol (70:25:5 by vol) before injection. The IPR consisted of 0.75 g of tetrabutyl ammonium acetate and 7.7 g of ammonium acetate in 100 ml of water. Analytical separation was achieved by isocratic delivery (1.5 ml min⁻¹, 21,000 kPa)

of mobile phase A (10% IPR in methanol) for 1.5 min, followed by a linear ramp to 100% B (27% acetonitrile) over 7 min and isocratic hold for an additional 12.5 min. The column was re-equilibrated between samples by linear ramping to 100% A over 7 min and maintenance for 4.5 min before sample injection. Samples were scanned for absorbance at both 660 and 430 nm (Fig. 1). In 1986, β -carotene coeluted with pheophytin *a* in several samples from Peter and Tuesday Lakes. For these dates only, β -carotene concentrations were not calculated and pheophytin *a* was quantified from scans at 660 nm.

The HPLC system was calibrated with a dilution series of each chromatographically pure pigment, where the amount of pigment in each standard was determined spectrophotometrically (Davies 1976). Specific extinction coefficients were obtained from Davies (1976), Foppen (1971), and Brown (1968). Pigment identifications were based on comparisons of the spectral characteristics and chromatographic mobility of pigments isolated from samples with those of pigments from unialgal cultures (*see below*) and published values (Wright and Shearer 1984). Pigments from all sources were isolated from elutant, diluted 50% with water, and collected on Waters C₁₈ Sep-Pak cartridges. Spectra were obtained and compared in acetone, methanol, ethanol, hexane, and diethyl ether (Chl only) with matched quartz cuvettes and a Beckman model DU-7 recording spectrophotometer.

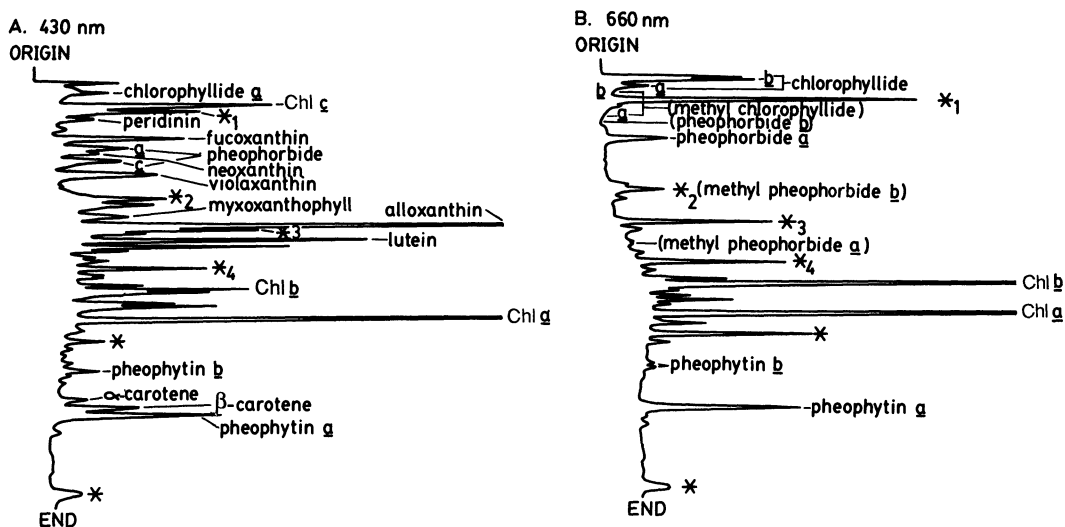


Fig. 1. Typical chromatographic separation of pigments from hypolimnetic water and sediment traps. Position of other chlorophyllous pigments indicated in parentheses. Asterisks denote unidentified Chl derivatives. Asterisk subscripts refer to spectra in Fig. 5.

The chromatographic mobility and light extinction characteristics of the pigments were compared to those listed by Mantoura and Llewellyn (1983), Davies (1976), Foppen (1971), and Wright and Shearer (1984). Epoxy-carotenoids were further identified by bathochromic spectral shifts caused by mild acidification (1 drop of 1 N HCl in 1 ml of ethanolic isolate; Liaaen-Jensen 1971; Davies 1976). Ketonic carotenoids and myxoxanthophyll were subject to NaBH_4 -catalyzed reduction and chromatographic and spectral reanalysis (Liaaen-Jensen 1971; Hertzberg et al. 1971).

Chl *a* and *b* derivatives were created by extracting *Poa pratensis* with either 50% aqueous acetone or methanol to produce acid or methyl chlorophyllides and acidifying (1 h, 5% solution of 1 N HCl) to convert them to their respective pheophorbides (N. Welschmeyer pers. comm.). Pheophytin derivatives and pheophorbide *c* were produced by acidification (as above) of pure Chl samples obtained from either Sigma Chemical Co. or extracts of *P. pratensis* or *Fucus* sp.

Unialgal cultures were obtained from either Carolina Biological Supply, the University of Texas culture collection (UTEX), or isolation from natural populations

(Leavitt and Brown 1988). When necessary, algae were cultured following the procedures of Leavitt and Brown (1988). Cultures used as pigment sources included: cyanophytes *Synechococcus* spp. (UTEX 1191, 563, 625) and *Coccochloris penicocystis* (UTEX 1548) (β -carotene, zeaxanthin sources), as well as *Oscillatoria limnetica*, *Oscillatoria utermoehlii* (β -carotene, echinenone, zeaxanthin, myxoxanthophyll), and *Anabaena flos-aquae* (canthaxanthin, 4-keto-myxol-2'-methylpentoside); a dinoflagellate *Peridinium cinctum* (peridinin); chlorophytes *Chlamydomonas reinhardtii*, *Ulothrix* sp., and *Micrasterias* sp., and euglenophyte *Trachleomonas* sp. (β -carotene, α -carotene, violaxanthin, neoxanthin, lutein); Chrysophyta *Synedra* sp. and *Ochromonas danica* (fucoxanthin, Chl *c*; also from *Fucus* sp.); and cryptophyte *Cryptomonas ovata* (UTEX 358) (alloxanthin).

Only those major carotenoids that are taxonomically diagnostic at the algal division level were quantified. Mean first-order decay constants (k , d^{-1}) were calculated as

$$k = \frac{\sum \left[\frac{\ln(P_t/P_i)}{\Delta t} \right]}{n}$$

Table 2. Pigment degradation constants (k , equation given in text) and initial concentrations in 1986. Lakes: L—Paul; T—Tuesday; R—Peter. Pheophorbide—Pheob; pheophytin—Pheo. Asterisk: k significantly different from 0, two-tailed t -test, $P < 0.05$.

Duncan's grouping†				P	Decay constant (k , d^{-1})	Lake	Pigment	Initial (nM)			
		A		*	0.0239	L	Pheob <i>c</i>	0.344			
	B	A			0.0061	T	Chl <i>a</i>	0.199			
	B	A		*	0.0058	T	β -carotene	0.0394			
	B	A		*	0.0058	T	Chl <i>b</i>	0.290			
	B	A			0.0051	T	alloxanthin	0.389			
	B		C		0.0019	T	lutein	0.0429			
	B		C	D	0.0004	L	β -carotene	0.373			
	B	E	C	D	-0.0019	T	Pheob <i>a</i>	0.449			
F	B	E	C	D	*	-0.0058	L	lutein	0.760		
F	B	E	C	D	*	-0.0070	T	fucoxanthin	0.133		
F	B	E	C	D	*	-0.0091	L	alloxanthin	9.44		
F	B	E	C	D		-0.0099	T	Pheob <i>b</i>	0.0560		
F	B	E	C	D	*	-0.0100	T	Pheo <i>a</i>	2.05		
F	B	E	C	D	*	-0.0123	R	β -carotene	0.0312		
F	B	E	C	D		-0.0128	L	Pheob <i>a</i>	3.72		
F	B	E	C	D	G	*	-0.0141	L	Pheo <i>b</i>	0.417	
F	B	E	C	H	D	G	*	-0.0163	L	Chl <i>b</i>	2.86
F		E	C	H	D	G		-0.0206	T	Pheo <i>b</i>	0.0188
F		E	C	H	D	G	*	-0.0213	L	Pheo <i>a</i>	18.8
F		E		H	D	G	*	-0.0224	R	Pheob <i>a</i>	0.498
F		E		H		G	*	-0.0249	R	fucoxanthin	0.470
F		E	I	H		G	*	-0.0255	R	Pheob <i>c</i>	0.0308
F	J		I	H		G	*	-0.0286	L	fucoxanthin	2.46
	J		I	H	K	G	*	-0.0357	R	alloxanthin	0.627
	J	L	I	H	K	G	*	-0.0362	R	Chl <i>c</i>	1.00
	J	L	I	H	K		*	-0.0390	R	lutein	0.0809
	J	L	I		K		*	-0.0463	L	Chl <i>a</i>	6.21
	J	L			K		*	-0.0503	R	Pheo <i>a</i>	1.43
		L			K		*	-0.0518	R	Chl <i>b</i>	0.0980
		L			K		*	-0.0526	L	Chl <i>c</i>	9.50
		L			K		*	-0.0582	R	Chl <i>a</i>	0.345

† Means with the same letter are not significantly different ($P > 0.05$).

where P_t is the pigment concentration (nmol liter⁻¹) at time t , P_i the initial pigment concentration, Δt the time elapsed in incubation (in days), and n the number of independent estimates. Therefore, k is negative when pigments decayed during the experiment and positive when pigments accrued during the experiment. Decay constants were compared between pigments and lakes for each year with Duncan's multiple range test (critical $\alpha = 0.05$). Individual decay constants were tested for significance ($H_0: k = 0$) with a two-tailed Student's t -test ($P = 0.05$).

Pigment degradation differed among lakes in both years (Figs. 2, 3; Tables 2, 3). In instances where a pigment occurred in all lakes, its losses were usually greatest in Peter Lake (7 of 9 pigments, both years), although

the differences were not always statistically significant (Tables 2, 3). In 1986, the exceptions to this pattern were pigments characteristic of the Chrysophyta (fucoxanthin, Chl *c*), which degraded most rapidly in Paul Lake. Similarly, mean decay constants were usually smallest in Tuesday Lake in 1986 (8 of 9 pigments), but not in 1987 (3 of 10).

Patterns of pigment loss with time were broadly divided into four categories: increased concentrations (pheophorbide *c*, Fig. 4), low rates of change (Tuesday Lake 1986, Paul Lake 1987), rapid loss followed by stable concentrations (biphasic degradation) (Peter Lake 1986), and logarithmic pigment losses with time (Peter Lake 1987). Decomposition in 1986 was poorly described by logarithmic relations and the lack-of-fit statistic was frequently significant in linear

Table 3. As Table 2, but for 1987.

Duncan's grouping†		P	Decay constant (k, d ⁻¹)	Lake	Pigment	Initial (nM)
	A	*	0.0883	T	Pheob <i>b</i>	0.0347
	B		0.0196	R	Pheob <i>a</i>	0.424
C	B	*	0.0190	L	Chl <i>c</i>	3.39
C	B	*	0.0185	T	β -carotene	0.116
C	B	*	0.0172	L	β -carotene	0.605
C	B		0.0148	L	Pheob <i>b</i>	0.474
C	B		0.0089	T	Chl <i>c</i>	1.51
C	E		0.0033	T	myxoxanthophyll	0.408
C	E		0.0028	T	fucoxanthin	0.329
F	C		0.0009	L	lutein	1.21
F	C		-0.0043	L	Chl <i>b</i>	7.02
F	C		-0.0050	R	Chl <i>b</i>	0.566
F	C		-0.0057	L	Pheo <i>a</i>	3.34
F	C		-0.0136	L	alloxanthin	30.3
F	C		-0.0154	L	fucoxanthin	2.90
F	C		-0.0165	T	Pheo <i>a</i>	0.936
F	C		-0.0167	R	β -carotene	0.144
F	C		-0.0233	T	Pheob <i>a</i>	1.03
F	C		-0.0242	R	fucoxanthin	1.43
F	C		-0.0266	T	Chl <i>a</i>	3.02
F	C		-0.0269	R	myxoxanthophyll	0.431
F	C		-0.0286	L	Pheob <i>a</i>	4.05
F	C		-0.0370	L	Chl <i>a</i>	11.5
F	C		-0.0370	T	Pheo <i>b</i>	0.0313
F	C		-0.0422	T	lutein	0.413
F	E		-0.0457	L	Pheo <i>b</i>	0.251
F	E		-0.0494	R	Pheo <i>a</i>	1.303
F	E		-0.0494	T	Chl <i>b</i>	0.955
F	I		-0.0592	R	alloxanthin	2.91
	I		-0.0609	T	alloxanthin	5.33
	I		-0.0652	R	Chl <i>c</i>	2.13
J	I		-0.0843	R	peridinin	0.598
J	I		-0.0870	R	lutein	0.238
J			-0.1226	R	Chl <i>a</i>	3.31

† Means with the same letter are not significantly different ($P > 0.05$).

regressions of both untransformed and log-transformed relative concentrations vs. time. Graphs indicated either slow pigment degradation or biphasic decomposition wherein rapid initial loss rates were sharply reduced after 50 d (Fig. 2). Similar patterns were noted in Paul and Tuesday Lakes in 1987; pigment concentrations declined logarithmically in Peter Lake in 1987 (Fig. 3). Few native pigments (carotenoids, Chl *a*, *b*, *c*) accumulated during the experiments (Tables 2, 3).

Two-way ANOVA of transformed data showed that both time and initial oxygen levels were significant ($P < 0.05$), synergistic ($P < 0.05$) determinants of the extent of degradation for all carotenoids and most chlorophyllous pigments in both years. These factors could not account, however,

for all patterns of observed decay. For example, in 1986 losses of the pigments characteristic of the Chrysophyta (fucoxanthin, Chl *a*, *c*) were more similar in Paul and Peter Lakes than in Paul and Tuesday Lakes, despite the similarity in both oxygen tension and degradation of the other pigments in the latter two lakes (Fig. 2). These results may simply reflect the overall lack of pigment decay in Tuesday Lake in 1986. Alternately, differences in initial algal communities and detrital composition may affect rates of pigment loss. In all lakes, epilimnetic chrysophyte communities were dominated by *Mallomonas caudata*, while Tuesday Lake also had a metalimnetic community composed largely of *Dinobryon cylindricum* (Table 2).

Decomposition of native pigments dif-

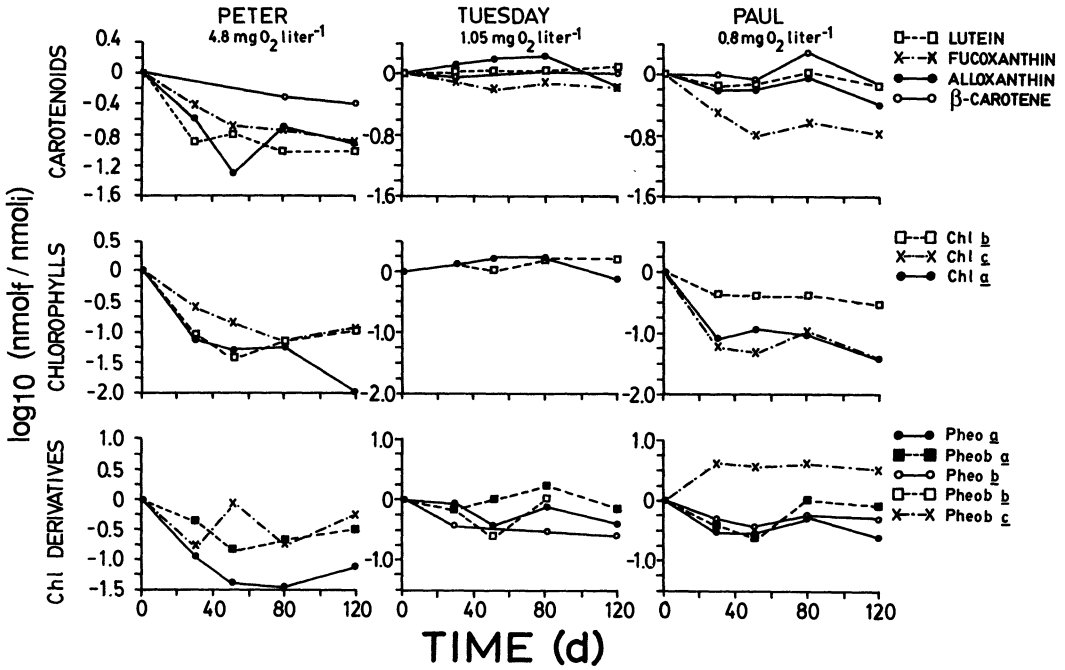


Fig. 2. Initial oxygen levels (mg liter⁻¹) and log of relativized changes in carotenoid, Chl, and Chl derivative concentrations in hypolimnetic incubations in Peter, Tuesday, and Paul Lakes in 1986. Each point is the mean of triplicate determinations, except β-carotene in Tuesday and Paul Lakes (1–3 determinations). Standard errors usually <10% of mean. Pheophytin—Pheo; pheophorbide—Pheob.

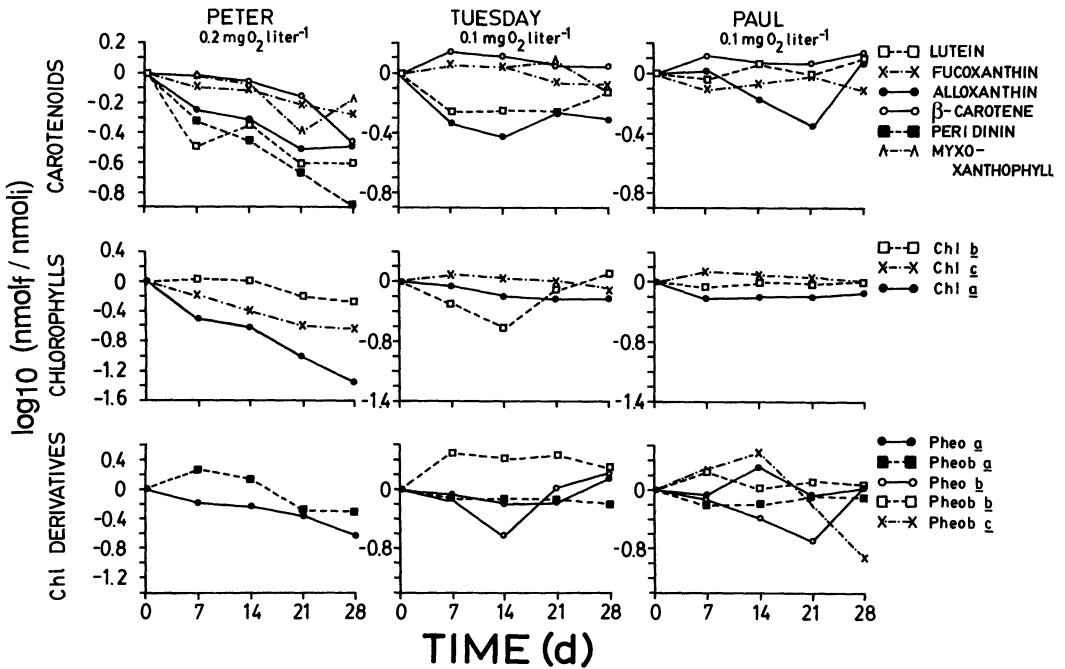


Fig. 3. As Fig. 2, but for 1987.

ferred qualitatively within lakes, between years. In Paul Lake, most native pigments degraded faster in 1986 than in 1987 (6 of 7 pigments); the reverse was true in Peter Lake (5 of 7) and, to a lesser extent, in Tuesday Lake (4 of 6). Half of all pigment-lake combinations (e.g. β -carotene in Peter Lake) showed greater decomposition in 1986 for both carotenoids and chlorophylls; pheopigments, however, generally degraded faster in 1987 (7 of 9).

Chl *a* decay spanned a wide range ($k = +0.0061 \text{ d}^{-1}$ to -0.1226 d^{-1}), with losses maximal in Peter Lake and least in Tuesday Lake in both years (Tables 2, 3). Except for Tuesday Lake in 1986 (no decay), Chl *a* degradation exceeded that of most other pigments in a given lake and year, although pairwise differences were not always statistically significant. No distinct trend was noted among different chlorophylls: Chl *b* was least degraded in some instances (Paul Lake 1986, Peter Lake 1987), and Chl *c* was either marginally more stable in others (Peter Lake 1986, Tuesday Lake 1987) or the most degraded Chl (Paul Lake 1986).

Chl *a* and *b* degradation was usually not compensated by production of either acid or methyl pheopigment derivatives. They contrast with Chl *c*, which showed concurrent production of pheopigments in most experiments (Fig. 4), although these increases did not compensate stoichiometrically for Chl *c* losses. Interestingly, slight increases in Chl *c* occurred in Paul Lake in 1987 (Table 3), despite pheophorbide *c* production. Rates of pheophytin *a* and pheophorbide *a* loss were similar in all instances, except Peter Lake in 1986 (Fig. 2). Co-occurrence of both *b*-phorbin derivatives was infrequent, making comparisons of the relative rates of pheophytin *b* and pheophorbide *b* degradation impossible.

Most samples were characterized by an abundance of unidentified, Chl-like pigments (Figs. 1, 5). These unknown pigments were absent from epilimnetic waters, increased in concentration with depth, and reached maximal concentration in recently deposited sediments (Leavitt and Carpenter unpubl. obs.). Although certain derivatives appear to be pheophorbide *a* degradation products (Fig. 5B) similar to those found in

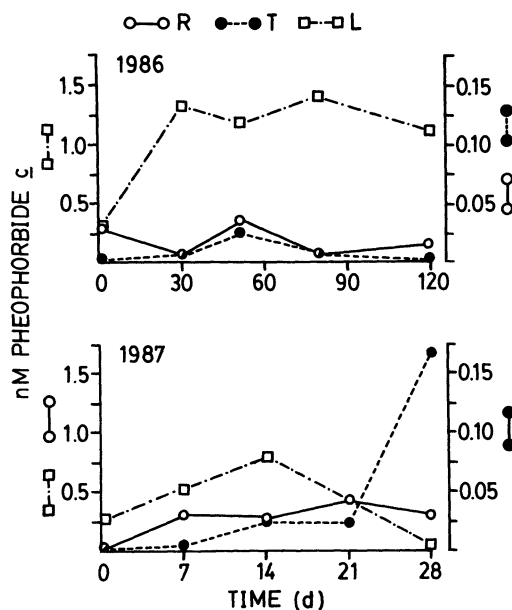


Fig. 4. Production of pheophorbide *c*. Peter Lake—R; Tuesday Lake—T; Paul Lake—L.

other freshwater and marine systems (Vermet and Lorenzen 1987; Hurley 1988; Furlong and Carpenter 1988), others are *b*-phorbinlike (Fig. 5C,D) or completely unknown (Fig. 5A). Their pattern of abundance in Peter, Paul, and Tuesday Lakes suggests that the unknown pigments are degradation products, although no distinct trend (production or degradation) was noted in these experiments.

In each lake, β -carotene was among the least degraded pigments (Figs. 2, 3; Tables 2, 3). Consequently, xanthophyll degradation always exceeded that of β -carotene in a given lake, although differences were frequently not statistically significant. Trends among xanthophylls were less distinct. Alloxanthin (cryptophytes) and lutein-zeaxanthin (green algae/blue-greens) were never significantly different ($P > 0.05$), as expected due to their structural similarities. Peridinin was very poorly preserved in the sole experiment where it occurred (Peter Lake, 1986), whereas myxoxanthophyll degraded relatively slowly. Fucoxanthin exhibited the most variable losses relative to the other carotenoids (e.g. Fig. 2, Tuesday vs. Paul Lakes).

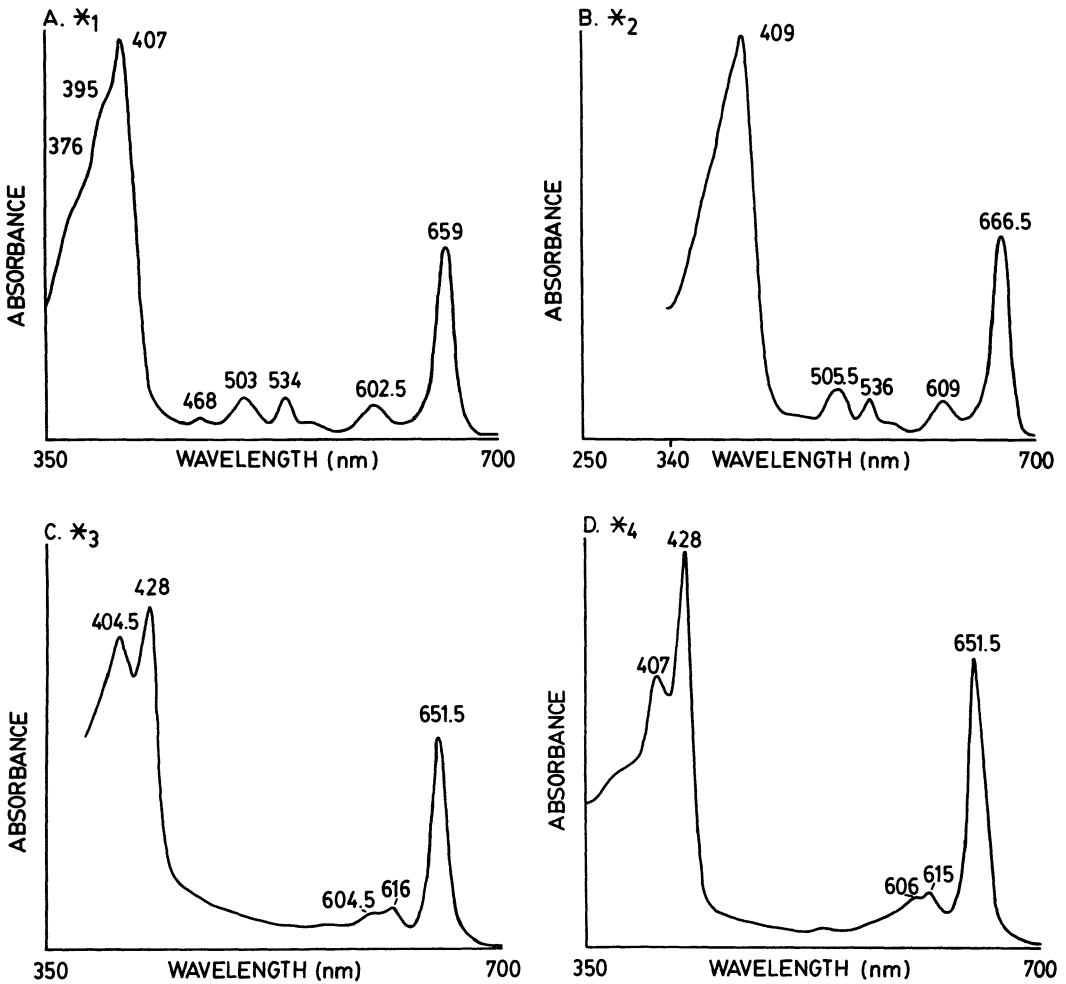


Fig. 5. Absorbance spectra of unidentified chlorophyllous pigments in diethyl ether.

Pigment degradation varied substantially both among lakes, within years and between years, within lakes (Figs. 2, 3; Tables 2, 3). Patterns of pigment loss (logarithmic, biphasic, negligible) varied similarly among experiments. Generally, losses were greatest in Peter Lake (biphasic in 1986, logarithmic in 1987) and least in Tuesday Lake (1986) or Paul Lake (1987). Experimental design excluded any effects of light, temperature, and the dominant macrograzer (*Daphnia*). Therefore, losses result from a combination of chemical, bacterial, and microfaunal effects. Variability among experiments may result from differences in these factors, as

well as species specificity in the rates of algal decomposition. Significant increases in a few native pigments (Tables 2, 3) may result from compensatory production of pigment by algae as a consequence of transfer from a low-light environment (<1% incident irradiance) to an aphotic bottle (Goodwin 1980). These increases appear short lived (Figs. 2, 3), but suggest that our decay constants may document net pigment losses and represent minimal estimates of the importance of degradation in the hypolimnion.

Two-way ANOVA identified both time and initial oxygen concentration as significant ($P < 0.05$) covariates of the extent of

Table 4. Dominant phytoplankton species (% total biovolume) before the experiment. Species tabulated only if >1% total cell abundance and >1% total biovolume. Note that columns do not add to 100% because of numerous rare species (e.g. dinoflagellates). Epi—epilimnetic community; Meta—metalimnetic community. Relative abundance tabulated independently for each community.

	Peter		Paul		Tuesday	
	Epi 0–3.5 m	Meta 4.5 m	Epi 0–2.0 m	Meta* 3.75 m	Epi 0–1.0 m	Meta 2.75 m
1986						
<i>Anabaena circinalis</i>	33.6	35.3	11.2	16.1	—	—
<i>Merismopedia tenuissima</i>	—	—	—	4.3	—	—
<i>Microcystis aeruginosa</i>	—	—	—	3.5	—	4.1
<i>Cryptomonas ovata</i>	19.6	31.6	17.4	9.9	22.8	36.2
<i>Rhodomonas minuta</i>	1.1	—	—	—	—	—
<i>Chrysochromulina</i> sp.	—	—	—	—	1.9	—
<i>Dinobryon cylindricum</i>	—	—	—	—	—	42.8
<i>Mallomonas caudata</i>	25.1	—	40.3	—	16.9	—
<i>Synedra</i> sp.	—	—	7.1	—	—	—
<i>Gleocystis</i> sp.	—	2.0	—	20.9	—	—
<i>Oocystis lacustris</i>	6.5	1.2	2.5	23.1	—	6.1
<i>Quadrigula lacustris</i>	—	—	—	—	1.3	—
<i>Schroederia setigera</i>	3.3	—	—	—	43.0	—
<i>Sphaerocystis shroeteri</i>	—	16.2	—	—	—	—
Misc. microflagellates	6.2	7.7	14.0	6.8	7.2	2.8
1987						
<i>A. circinalis</i>	3.5	8.4	3.9	14.1	—	—
<i>Aphanocapsa</i> sp.	—	6.6	—	—	—	—
<i>Chroococcus limneticus</i>	3.0	—	—	—	—	—
<i>M. tenuissima</i>	—	—	3.0	6.3	—	—
<i>Oscillatoria</i> sp.	—	—	—	—	2.9	—
<i>C. ovata</i>	10.7	4.4	13.2	1.1	7.0	2.4
<i>R. minuta</i>	2.3	2.5	—	—	—	3.4
<i>Asterionella formosa</i>	8.8	7.9	—	—	—	—
<i>Dinobryon divergens</i>	43.5	14.8	6.1	—	—	—
<i>M. caudata</i>	—	—	5.6	—	—	—
<i>Synura</i> sp.	—	—	—	5.2	—	—
<i>O. lacustris</i>	12.0	7.6	—	—	—	—
<i>Trachelomonas</i> sp.	—	—	—	—	28.4	—
Misc. microflagellates	6.0	20.0	7.6	8.0	20.1	11.7

* Depth 4.0 m for 1987.

pigment decay. Acceleration of decay by oxygen has been demonstrated in vitro in studies of both carotenoid (Cranwell 1976; Leavitt 1988) and algal decomposition (Otsuki and Hanya 1972a,b) and results from stimulation of bacterial degradative activities or establishment of different microbial species (Leavitt 1988). Such microbially mediated carotenoid degradation appears to proceed through dehydration reactions (Repta and Gagosian 1984).

Some in vitro studies show that oxygen acts to degrade carotenoids directly (El-Tinay and Chichester 1970; Davies 1976; but see Leavitt 1988). Comparison of decay kinetics in 1986 and 1987 suggests that oxy-

gen effects can be indirect and act through stimulation of either bacterial or microfaunal activities. If oxygen acts directly, then pigment decomposition in Tuesday Lake in 1986 ($1.05 \text{ mg O}_2 \text{ liter}^{-1}$) should exceed that in 1987, regardless of the lake (all lakes $<0.2 \text{ mg O}_2 \text{ liter}^{-1}$). Instead, alloxanthin decay was nonsignificant in Tuesday Lake 1986 ($k = +0.0051 \text{ d}^{-1}$, Table 2), yet was always significant in 1987 ($k = -0.0136$ to -0.0609 d^{-1} , Table 3). Because all cryptophyte communities were dominated by *C. ovata* with lesser amounts of *Rhodomonas minuta* (Table 4), species-specific differences in algal decay cannot explain the observed trends, and interlake differences must be due to dif-

ferences in heterotrophic community composition or activity.

Other differences in the chemical environments of the lakes may have regulated bacterial activity and, hence, pigment degradation. Both acidic waters and humic substances repress microbially mediated degradation of organic compounds (Wetzel 1983). In both years, pigment losses were greatest in Peter Lake—the most alkaline and least-stained lake (Table 1). Pigment degradation was slowest in Tuesday Lake—the most acidic, stained lake—both in 1986 and for some pigments in 1987.

Because phytoplankton community composition varied considerably below the division level (Table 4), it is not possible to eliminate effects of community composition on differences in pigment degradation. For example, in 1986 losses of pigments characteristic of the Chrysophyta (fucoxanthin, Chl *c*) were much greater in Paul Lake than Tuesday Lake, despite similarity in oxygen levels and decay of other pigments. Although these differences may reflect the general lack of pigment loss in Tuesday Lake, it is also possible that pigments in *Dinobryon divergens*, the Tuesday Lake codominant, degrade less rapidly than those of *M. caudata*, which is an important alga in all lakes. Species-specificity in rates of carotenoid and Chl loss have been shown during in vitro decomposition of various algae (Daley and Brown 1973; Cranwell 1976; Owens and Falkowski 1982).

The most informative comparisons of pigment loss are those within lakes. Regardless of the ultimate cause of pigment degradation (oxygen, bacterial, microfaunal), these experiments mimic the conditions in which detrital particles sink and sediment traps are commonly suspended. Consequently, the rapid and variable losses seen here have important implications for both sedimentation studies and paleolimnology.

Chl *a* decay was highly variable ($k = +0.0061 \text{ d}^{-1}$ to -0.1226 d^{-1}). Except for the nonsignificant changes in Tuesday Lake in 1986 ($k = +0.0061 \text{ d}^{-1}$, t -test $P > 0.05$), however, Chl losses were always significant ($P < 0.05$) and generally significantly ($P < 0.05$, Duncan's multiple comparison) and

substantially greater than those of many other pigments (Tables 2, 3). Chl *a* decay constants are similar to those of other chlorophyllous pigments calculated indirectly from comparisons of sediment trap catch and surficial sediments (Furlong and Carpenter 1988), but are lower than photo-oxidation constants (Welschmeyer et al. 1985*a,b*; Carpenter et al. 1986). Because viable cells rapidly replace photo-oxidized Chl *a* and herbivores convert Chl *a* to pheopigments, our results suggest that hypolimnetic decay of native Chl *a* is the most significant determinant of Chl *a* flux to and concentration in lacustrine sediments. Consequently, much of the variability in the relationship between Chl standing stocks and sedimentary abundance of Chl *a* and its derivatives may result from lake-specific differences in the rate of aphotic, hypolimnetic Chl *a* decay (e.g. Brenner and Binford 1988; Downing and Rath 1988). The importance of hypolimnetic decay will depend on both the depth of the oxic zone relative to the maximal depth of the lake and the position of the algal population within the oxic zone (see below).

Use of Chl *a* as a sedimentation indicator is further complicated by two factors. First, decay of Chl *a* is not compensated by production of either acid or methyl pheopigment derivatives, in contrast to Chl *c* (Fig. 4). Therefore, the use of acidification ratios in fluorometric or spectroscopic studies (to estimate Chl conversion to pheophytin *a* or pheophorbide *a*) will not "recover" lost Chl *a*. This fact may lead to substantial underestimation of algal flux from the water column. Second, all deep-water samples contained several abundant, unknown pigments that have absorption spectra similar to Chl *a* (Figs. 1, 5). The concentrations of these chlorophyllous pigments increase with depth below the lake surface, suggesting that they are decomposition products. Because these compounds were not produced in our experiments, however, their sources remain unknown. Until their fluorescence and light extinction characteristics are established, their contribution to estimates of algal sedimentation and sedimentary pigment concentrations (as sedimentary Chl degradation products, SCDP, Daley et al. 1977)

remains unknown. Similar chlorophyllous pigments are common in marine waters (Gieskes and Kraay 1983; Vernet and Lorenzen 1987; Furlong and Carpenter 1988) and freshwater sediments (Daley et al. 1977).

In contrast to Chl *a*, β -carotene losses were both less rapid and less variable ($k = +0.0185 \text{ d}^{-1}$ to -0.0167 d^{-1}). In lakes where Chl *a* decay was significant (i.e. $k < 0$, $P < 0.05$), Chl *a* degradation was substantially greater than that of β -carotene (Chl $k - \beta$ -carotene $k = -0.0467 \text{ d}^{-1}$ to -0.1059 d^{-1}). Further, in each lake β -carotene was among the least labile pigments (Tables 2, 3). β -carotene stability presumably results from the absence of reactive, oxygen-containing functional groups on the carotenoid (Brown 1969). Therefore, because β -carotene is ubiquitous in algae (Goodwin 1980), it will be a superior indicator of total algal sedimentation. Variability among algal taxa in the cellular content of β -carotene (Goodwin 1980) and Chl *a* (Reynolds 1984) is similar.

Differences in degradation between Chl *a* and β -carotene have important implications for sedimentation studies. For example, if we use decay constants from 1987 (Table 3) and phorbins composition in sediment traps from Carpenter et al. (1988), we can calculate bias in sedimentation estimates for extreme conditions of either slow decay (Tuesday Lake, 1987) or rapid pigment loss (Peter Lake, 1987). If decay follows first-order kinetics and daily pigment inputs to traps are constant over the period of deployment, pigment dynamics in the traps follow

$$dp/dt = s + kp \quad (1)$$

where p is the pigment content of the trap ($\mu\text{mole m}^{-2}$), s the daily input rate ($\mu\text{mole m}^{-2} \text{ d}^{-1}$), t the time (days) and k the hypolimnetic decay constant (d^{-1}). Under the initial condition that $p = 0$ when $t = 0$, the solution of Eq. 1 is

$$s = pk/[1 - \exp(tk)]. \quad (2)$$

When the duration of trap deployment (t) and final pigment content of the trap (p) are substituted in Eq. 2, the daily decay-corrected pigment input (s) can be calculated. The total decay-corrected trap catch is cal-

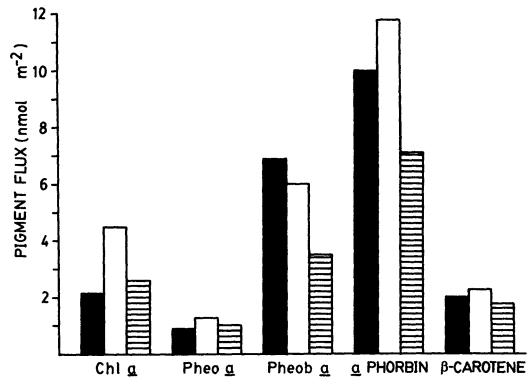


Fig. 6. Hypothetical sediment trap catch after 2-week deployment. Black—measured (observed) catch; white—catch corrected with Peter Lake 1987 decay coefficients (k_R); striped—catch corrected with Tuesday Lake 1987 coefficients (k_T). *a* phorbins include Chl *a*, pheophytin *a* (Pheo *a*), and pheophorbide *a* (Pheob *a*). Initial phorbins composition: 21.6% Chl *a*, 9.2% pheophytin *a*, 69.2% pheophorbide *a* (total $10 \mu\text{mol m}^{-2}$), and $2 \mu\text{mol m}^{-2}$ β -carotene.

culated by multiplying s by the length of trap deployment (t) in days.

Rapid pigment decay typical of Peter Lake resulted in $>50\%$ underestimation of Chl *a* accumulation, whereas slow degradation (Tuesday Lake) biased estimates 16% (Fig. 6). Estimates of sedimentation that used total phorbins accumulation were less variable (15–29% bias). In contrast, decay-corrected β -carotene deviated from observed pigment accumulation by $<12\%$, even with the fastest decay coefficients we observed. This pattern suggests that β -carotene is a superior estimator of algal sedimentation and may be useful in eliminating some of the variation in relations between pigment standing stock (“production”) and sedimentary pigment concentrations (e.g. Brenner and Binford 1988; Downing and Rath 1988).

Corrected sedimentation rates derived from Eq. 2 can also be used to correct Chl budgets for hypolimnetic decay (Carpenter et al. 1986, 1988). This correction will increase sedimentation estimates and therefore increase estimates of nonplanktonic pigment input (equation 6 of Carpenter et al. 1986). Correction for hypolimnetic decay amplifies the apparent importance of large herbivores noted by Carpenter et al. (1986, 1988). Peter Lake, which had the

largest *Daphnia*, also has the largest correction for hypolimnetic decay (Fig. 6), and therefore the dependency of sedimentation on herbivore size seems even stronger than claimed by Carpenter et al. (1986).

In Tuesday Lake, large *Daphnia* were scarce in 1984 but dominant in 1985 (Carpenter et al. 1988). The shift in the zooplankton community was accompanied by increased pigment sedimentation (Carpenter et al. 1988). Traps were set in anoxic, aphotic water at 4°C for 7 d in 1984 and 14 d in 1985 (Carpenter et al. 1988), so the correction for hypolimnetic degradation was greater in 1985. Therefore, Carpenter et al. (1988) underestimated the magnitude of increase in sedimentation that followed the rise of large *Daphnia* populations. In sum, the qualitative conclusion that large herbivores cause high pigment sedimentation in these lakes remains correct, but the quantitative effect of large herbivores on sedimentation is greater than reported by Carpenter et al. (1986, 1988).

In each lake and year, xanthophyll loss was greater than carotene loss. This finding is consistent with paleolimnological studies (Sanger 1988), but not with some in vitro results (Leavitt 1988). Trends among xanthophylls are complex and only partially elucidated by our study. Structurally similar carotenoids (e.g. alloxanthin, lutein-zeaxanthin) decay identically, within the errors of detection. This kinetic similarity suggests that the overabundance of alloxanthin in both marine and freshwater sediments (Repeta and Gagosian 1987; Hurley 1988; Leavitt and Carpenter unpubl. obs.) does not result from large differences in alloxanthin decay kinetics. Excess sedimentary alloxanthin may result from preferential sedimentation of cryptophytes in zooplankton feces (cf. Carpenter et al. 1986, 1988).

Peridinin, a carotenoid characteristic of dinoflagellates, was very poorly preserved in the sole experiment where it occurred (Peter Lake in 1987, $k = -0.0843 \text{ d}^{-1}$), a result common in other freshwater studies (Hurley 1988). This lability is also consistent with marine studies that examined carotenoid losses in much different depositional environments (>240 m of water); complete pigment destruction was attrib-

uted to the presence of reactive 5,6-epoxides in peridinin and fucoxanthin (Repeta and Gagosian 1984, 1987). Interestingly, we do not find a consistent lability of fucoxanthin in all experiments, perhaps reflecting lake or taxon specificity in the importance of different loss processes. Similarly, myxoxanthophyll decomposition proceeds relatively slowly (Table 2), a finding that contrasts with the general observation that highly substituted carotenoids are extremely labile (Brown 1969; Hurley 1988).

Pigment-specific differences in carotenoid decomposition have important implications in paleolimnological studies. Many xanthophylls are taxonomically diagnostic, some to the division level or lower (Goodwin 1980). Unfortunately, our study shows that paleolimnological investigators will have difficulty in reconstructing absolute algal abundances (especially of dinoflagellates), even in small lakes with good conditions for pigment preservation. Comparisons of pigment catch in sedimentation traps and sedimentary pigment concentration support this view (Hurley 1988). Sedimentary pigment accumulation will be biased toward algae that form deep blooms or are otherwise rapidly removed from the oxic zone of a lake (e.g. in zooplankton feces). Thus, high sedimentary concentrations of undegraded chlorophylls may be more indicative of the presence of metalimnetic populations of phytoplankton than of high production (Swain 1985).

Fortunately, overall changes in production may be distinguished from deep blooms with Chl *a*: β -carotene ratios and xanthophyll indicators. As epilimnetic populations slowly sink through the oxic zone, Chl *a*: β -carotene ratios will decrease, due to preferential loss of Chl *a*, other factors being equal. This pattern may be similar regardless of the level of primary production, although the absolute extent of pigment loss may be inversely related to lake trophic status (see Leavitt and Brown 1988; Leavitt 1988). In contrast, large metalimnetic populations occur deep in the water column, tend to have simpler plankton compositions, and are sometimes dominated by a single species (e.g. Pick et al. 1984). Under the latter scenario, differential losses of Chl

a are reduced. Thus, in paleolimnological reconstructions, increases in productivity (or enhanced pigment preservation) will be reflected by nonspecific increases in concentrations of most pigments relative to prior (downcore) conditions (e.g. Züllig 1982; Sanger 1988), whereas metalimnetic blooms will be evident as increased Chl *a* concentrations and increased Chl *a*: β -carotene ratios. Individual, division-specific xanthophylls may be used to identify compositions of the metalimnetic populations. Therefore, relative (within-core) changes in the abundance of individual pigments remain important in paleolimnological studies.

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