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Global and Planetary Change 46 (2005) 29–44

GLOBAL AND PLANETARY CHANGE

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Flux of lipophilic photosynthetic pigments to the surface sediments of Lake Baikal

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Received 27 October 2003; received in revised form 29 June 2004; accepted 27 September 2004

Abstract

The pigment flux to the sediment surface was studied in Lake Baikal to evaluate the validity of approaches reconstructing long-term variations in standing crops of phytoplankton by fossil pigment analysis. Chlorophylls and carotenoids were analysed by HPLC in suspended and settling matter and in the surface sediment of the central south basin (c. 1400-m water depth). Sedimentation rates of dry matter, organic carbon and nitrogen were also determined. The flux of particulate matter in 40 m, directly below the euphotic zone, amounted to 14.9 g m^{-2} $month^{-1}$ with a carbon content of 21.9%, and an atomic C/N ratio of 14.8. The pigment flux was 12.1 μmol m^{-2} $month^{-1}$ chlorophyll *a*, 40.8 μmol m^{-2} $month^{-1}$ pheophorbide *a*, 6.5 μmol m^{-2} $month^{-1}$ pheophytin *a*, 2.1 μmol m^{-2} $month^{-1}$ chlorophyllide *a*, and 0.3 μmol m^{-2} $month^{-1}$ pyropheophytin *a*.

The decay during sedimentation can be described by two-exponential or decay regression models for organic carbon, total nitrogen, chlorophyll *a*, pheophorbide *a*, chlorophyllide *a*, chlorophyll *b*, and most carotenoids, but not for pheophytin *a*, pheophytin *b*, and pyropheophytin *a*. The two-phase character of the models outlined that, for the former components, the flux diminished strongly in a first phase down to 250-m water depth and remained rather stable below 250 m. The chlorophyll *a*/carbon ratio also decreased with depth, whereas the pheophytin *a*/carbon ratio and the pyropheophytin *a*/carbon ratio increased with depth. From chlorophyll *a*, plus its degradation products, 28% reached the lake bottom when compared to the sedimentation below the euphotic zone. Based on the marker pigments fucoxanthin, chlorophyll *b*, and zeaxanthin, the contribution of the main phytoplankton groups to the settled chlorophyll *a* was estimated as 87% Bacillariophyceae+Chrysophyceae, 11% Chlorophyta, and 2% cyanobacterial picoplankton. These relationships changed only little during the sedimentation through the whole water column, but diverged from compositions calculated for the summer standing crop.

Keywords: carotenoid; chlorophyll; organic carbon; phytoplankton; lake sediments; sediment traps

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doi:10.1016/j.gloplacha.2004.11.004

1. Introduction

Reconstructions of long-term climatic and environmental changes are based on several different biogenic proxies such as pollen, macrofossils, diatom valves, and lipophilic photosynthetic pigments preserved in the sediments (cf. Bennett et al., 2001). Traces of carotenoids, chlorophylls, and their degradation products persist long after the disappearance of morphologically distinguishable remains of the organisms that produced them (Brown, 1969) and are often the sole fossils of nonsiliceous algae (Leavitt, 1993). Several studies described pigment deposits in lake sediments, which were thought to be proxies of changing climate (Vinebrooke et al., 1998; Kowalewska, 2001; Soma et al., 2003), trophic states (Gorham et al., 1974; Adams and Prentki, 1986; Lami et al., 1994), anthropogenic influence such as sewage enrichment, land-use or dam building (Griffiths et al., 1969; Soma et al., 1995; Leavitt et al., 1999), lake acidification (Guilizzoni et al., 1992), UV radiation (Leavitt et al., 1997), stratification (Hodgson et al., 1998), or water-level fluctuations (Verschuren et al., 1999).

All algae and cyanobacteria contain chlorophyll *a*, but other chlorophylls and most of the carotenoids were found only in some taxonomic groups and can be used as marker pigments to quantify the relative importance of different chemotaxonomic groups in natural phytoplankton (Weber and Wettern, 1981; Gieskes et al., 1988; Everitt et al., 1990; Wilhelm et al., 1991; Wright et al., 1996 and others). However, several studies confirmed pigment-specific correlations between fossil pigments and historical data of the standing crop (Leavitt et al., 1989; Leavitt and Findlay, 1994; Hall et al., 1999; Bianchi et al., 2002). For instance, the ubiquitous pigments β-carotene and pheophytin *a* were correlated to total biomass (r=0.56–0.65) in the study of Leavitt and Findlay (1994) and the marker pigments lutein+zeaxanthin and pheophytin *b* were correlated to the biomass of Chlorophyta (r=0.53–0.55). In contrast, the marker pigments α-carotene and alloxanthin were only weakly correlated to Cryptophyta, and fucoxanthin and chlorophyll *c* were uncorrelated to Chrysophyta or Bacillariophyceae and peridinin to Dinophyta. The latter pigments were strongly degraded. Therefore, relative abundances of carotenoids in sediments might be an unreliable measure of former phytoplankton community composition and abundance (Leavitt, 1993).

The controversy whether changes in fossil pigment concentrations arose from changes in phytoplankton standing crop or degradation has been known for a long time (Brown, 1969; Swain, 1985; Sanger, 1988; Leavitt, 1993; Cuddington and Leavitt, 1999). Differential pigment degradation and losses during deposition in marine and fresh water depend mainly on (i) sinking rates that differ between species and between living and dead cells, (ii) selective meso- and microzooplankton grazing as well as different digestibility of cells, and (iii) light and oxygen availability during sedimentation (see reviews in Leavitt, 1993; Cuddington and Leavitt, 1999).

These processes of pigment degradation vary between lakes with different plankton community structures and lake morphometry. Therefore, lake-specific transfer functions should be established for a more substantiated interpretation of fossil pigment data. This is particularly relevant for the case of Lake Baikal, a unique ecosystem with many endemic species and a fully oxygenated water column depth comparable to marine systems.

The present study is part of the multidisciplinary paleoclimate project CONTINENT (EVK2-CT-2000-0057). The study reported here compares chlorophylls, pheopigments (degradation products of chlorophylls), and carotenoids of the standing crop with those collected in traps and on the lake bottom. The aim was to determine the pigment flux through the water column and to infer how the main phytoplankton groups were represented in the deposited material.

2. Methods and materials

During 16 months from 12th March 2001 to 5th July 2002, a sediment trap mooring, comprising 15 integrating traps, was deployed in the centre of the south basin (51°42′N/105°01′E), where water depth reached 1400 m. The traps were deployed approximately every 100 m. Only the uppermost trap was deployed at 40 m. Exact depths were determined after the recovery. The integrating traps were two acrylic cylinders with each an active area of 65 cm^2 and an aspect ratio of 1:8 (EAWAG-130, Ohlendorf and Sturm, 2001). After recovery of the traps, the

overlaying water was siphoned off and the sampling cups were covered with aluminium foil to avoid photo-degradation of the pigments. Duplicate subsamples of the suspended sediment trap material were filtered within 2 h upon recovery through Whatman GF/F-filters.

The top centimetre of the surface sediment was sampled and analysed to assess the pigment breakdown upon burial in the sediment. The core was taken in July 2002 at the mooring site, using a gravity corer (EAWAG-63) with PVC-liner (Ø=63 mm). The top centimetre at that site covered a time span of about 7 years (sedimentation rates of the core were determined based on excess activity of ^{210}Pb, measured with a CANBERRA well-type γ-detector; see also Müller et al., 2005-this volume).

All samples from sediment traps and surface sediment were immediately freeze-dried and stored frozen at −20 °C in the dark until analysis. Chlorophylls, carotenoids, and their derivatives were extracted with 1.25 mL of dimethylformamide under dim light at 4 °C. The extraction was done by vibration shaking with a frequency of 2000 min^{-1} over 3 h. A total of 125 μL of an ion-pairing reagent (IPR solution: 15 g L^{-1} tetrabutyl ammonium acetate and 77 g L^{-1} ammonium acetate) were added. The extract was centrifuged for 20 min at 4 °C at 5000×g in a cooled centrifuge (Biofuge Fresco, Heraeus Instruments, Hanau, Germany) and the supernatant was transferred in vials for HPLC-analysis.

The separation, identification, and quantification of pigments of all samples were done according to Woitke et al. (1994). The HPLC system (Waters, Milford, MA, USA) was composed of a Waters 717 autosampler, a Waters 616 pump, and a Waters 600S controller. Pigments were separated at a flow rate of 1.0 mL min^{-1} at 30 °C through a non-end-capped Waters Resolve C18 column (30 cm), protected with an appropriate precolumn, with an optimised gradient system. The first solvent was methanol/acetonitrile/IPR (45:45:10) and the second was acetonitrile/acetone (45:55).

The eluting peaks were monitored at 440 nm using a Waters 996 photodiode array detector and at 410/670 nm (excitation/detection wavelength) using a Waters 474 fluorescence detector. Pigments were identified by their relative retention times and by their absorption spectra. Unialgal cultures, standards, and literature data were used for comparison. Peak area integration allowed quantification with factors initially determined by Woitke et al. (1994, 1996) and checked for the present study with standards supplied by Sigma, Hoffmann-La Roche (Grenzach, Germany) or Carbon 14 Centralen (Hørsholm, Denmark).

Water samples at eight stations were collected in July 2001 to determine the pigment concentration in the euphotic zone of the south basin (cf. Fietz and Nicklisch, 2004). Samples were taken in 5 m water depth and at two stations additionally at 10 and 30 m depth. Duplicate water samples (1–2 L) were filtered through GF/F-filters (Whatman, Kent, UK). Treatment of the water samples was similar to that of the trapped material but extraction was done with a mixture of acetone, methanol, and water (80:15:5 by volume, Leavitt et al., 1989), whereby glass beads (0.75–1 mm) were added to the water samples to grind the filters, vibration shaking lasted for 1.5 h, and centrifugation was done at 2500×g. No significant difference was found for the extraction with dimethylformamide and the acetone/methanol/water mixture. The separation, identification, and quantification of the pigments were carried out using the same technique as for the sedimentary pigments.

The dry matter, particulate organic carbon, and total nitrogen in the sediment traps were also determined. For that purpose, the suspended samples of the trapped material were cooled stored until analysis. Total dry weight was determined after freeze-drying of the samples. The carbon and nitrogen contents were determined with a EURO-EA® CNS-analyser. No significant differences were found between these analyses and analyses of five samples, which were centrifuged and freeze-dried on ship, and stored frozen.

All pigments could be assigned to various phytoplankton groups. In this study, we followed the taxonomic system of van den Hoek (1993) but used class or family names according to the respective pigment compositions. In that way, we used "Bacillariophyceae plus Chrysophyceae" because both families contain the marker pigments fucoxanthin and chlorophyll *c*, while other families of their class "Heterokontophyta" do not contain these markers. In addition, we used "Chlorophyta" because all phytoplankton families of this class contain the same pigment composition, but we used "cyanobacterial

picoplankton“ that clearly dominate the Baikalian cyanobacteria (Fietz and Nicklisch, 2004), because of their marker pigments zeaxanthin and caloxanthin, not prominent in filamentous cyanobacteria.

Principal components analysis (PCA) and standard deviations (S.D.) were calculated with SPSS© statistical package (SPSS, Chicago, Illinois, USA). Curve fittings were performed with TableCurve 2D® (Systat Software, Point Richmond, CA, USA).

3. Results

3.1. Pigments detected in the water column, sediment traps and surface sediments

Through the upper water column (water samples), the deeper water column (sediment traps) and also within the water/sediment interface (top sediment slice) major lipophilic photosynthetic pigments known from freshwater samples were detected by the HPLC-aided analysis (Table 1). Characteristic fluorescence and absorption chromatograms are shown in Fig. 1 for the water samples (Fig. 1A), the 40-m trap (Fig. 1B), the 1400-m trap (Fig. 1C), and the top sediment slice (Fig. 1D). Whereas most pigments were found in all samples, some were found only in the water samples (e.g., antheraxanthin), in the traps (e.g., chlorophyllide *a*), or in the sediment (e.g., canthaxanthin). Pheopigments, degradation products of chlorophylls, were found only in sedimented material (Fig. 1 and Table 1). Four different pheophorpide *a*-like pigments were found (Fig. 1). The occurrence of those pheophorpide *a* derivates was not correlated with the depth. Thus, all of them are grouped as “pheophorpide *a*” in the following text. All pheophytin *a*-like pigments were also grouped to “pheophytin *a*” in the text below. Pyropheophorbide *a*, which differs from pheophorpide *a* only by the elimination of a methylated carboxyl group from the isocyclic ring (Head and Horne, 1993), was also attributed to pheophorpide *a* as no respective standard was available. Pyropheophytin *a*, in contrast, could be clearly differentiated from pheophytin *a* and is

Table 1
Major lipophilic photosynthetic pigments in the euphotic zone (integration over 40 m water depth) as well as flux to the 40-m trap, to the trap at the lake bottom, and into the topmost sediment sample

No.	Pigment	Euphotic zone	40-m trap	1400-m trap	Core top	Phytoplankton groups
		(μmol m^{-2})	(μmol m^{-2} month^{-1})			
1	Chlorophyll *a*	66	12.07	2.89	0.111	all classes
2	Chlorophyll *b*	7.6	0.53	0.11	0.027	Chlorophyta
3	Chlorophyll *c*	1.6	2.63	0.41	0.014	Bacillariophyceae, Chrysophyceae, Cryptophyta
4	Chlorophyllide *a*	–	2.13	0.68	–	all classes
5	Pheophorbide *a*	–	40.78	6.74	0.38	all classes
6	Pheophytin *a*	–	6.5	6.5	0.202	all classes
7	Pheophytin *b*	–	0.075	0.075	0.045	Chlorophyta
8	Pyropheophytin *a*	–	0.32	0.32	0.128	all classes
9	Fucoxanthin	10.4	11.60	1.55	0.095	Bacillariophyceae, Chrysophyceae
10	Violaxanthin	4.0	0.05	–	–	Chlorophyta, Eustigmatophyceae
11	Diadinoxanthin	2.0	0.57	0.26	0.024	Bacillariophyceae, Chrysophyceae
12	Diatoxanthin	–	1.44	2.00	0.001	Bacillariophyceae, Chrysophyceae
13	Alloxanthin	2.4	0.84	0.04	0.001	Cryptophyta
14	Lutein	8.0	0.40	0.06	0.002	Chlorophyta, (Eustigmatophyceae)
15	Zeaxanthin	31	1.38	0.1	–	Cyanobacterial Picoplankton, (Chlorophyta)
16	β-carotene	5.2	0.39	0.007	–	all classes

Values for the lake-bottom (1400 m) were extrapolated from the curve fittings shown in Figs. 2 and 3 for all pigments with exponential decrease (see also Table 5). For pheophytin *a*, pyropheophytin *a*, and pheophytin *b*, which did not show a significant decrease with depth, 40-m and lake bottom values were calculated as averages of all traps. For each pigment, the respective (and important) phytoplankton groups in Lake Baikal are given, although groups in parenthesis contain very low amounts of the pigment. Chlorophyll *a* included allo-, epimers, and other derivates; pheophorbide *a* included all pheophorbide *a* derivates; and pheophytin *a* included all pheophytin *a* derivates.

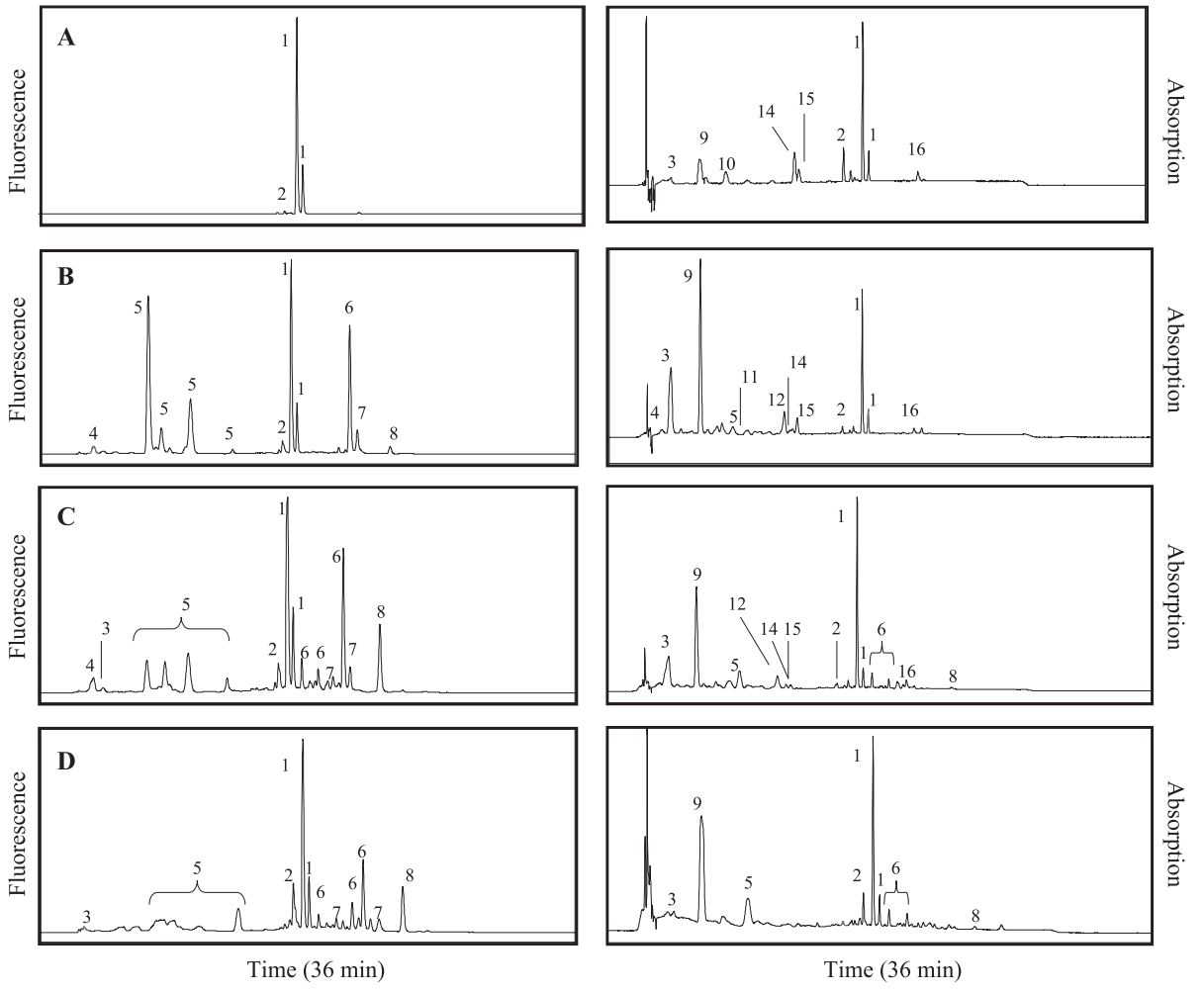

Fig. 1. Typical fluorescence (410 nm/670 nm excitation/detection wavelength, left side) and absorption (440 nm) chromatograms (right side) of (A) the water column, (B) the 40-m trap, (C) the 1400-m trap, and (D) the top sediment slice below the mooring. Numbering of the peaks confers to pigments listed in Table 1.

discussed separately (Fig. 1 and Table 1). The chromatograms of pigment extracts of the sediment traps and sediment slices also contained several unidentifiable components (unnumbered peaks in Fig. 1). They were strongly degraded pigments which were not included in our quantitative comparisons.

3.2. Pigments in the Euphotic Zone

Chlorophyll *a* was the most prominent pigment within the upper water column in the south basin (Fig. 1 and Table 1). Integrated over 40 m, the estimated chlorophyll *a* of the water column was 66 μmol m^{-2}, which corresponds to a mean concentration of 1.7 μmol m^{-3}. The amounts of distinct carotenoids were about one order of magnitude lower than chlorophyll *a*. The most prominent carotenoid was zeaxanthin (Zea, Table 1). Other prominent carotenoids were fucoxanthin (Fuco), chlorophyll *b* (Chl*b*), and lutein (Table 1). The amounts of β-carotene, chlorophyll *c*, and diadinoxanthin were much lower (Table 1). Alloxanthin was not found in all samples.

The following equation that was established in a previous study (Fietz and Nicklisch, 2004), was applied to estimate the contribution of the three main phytoplankton groups (Bacillariophyceae plus Chrys-

Table 2
Sedimentation and accumulation rates of the dry matter, total nitrogen, and atomic C/N ratio in the 40-m trap, at the lake bottom and in the topmost sediment sample

	40-m trap	1400-m trap	Core top
Dry weight ($g\ m^{-2}\ month^{-1}$)	14.9	9.49	7.41[a]
Organic carbon (%)	21.87	7.14	3.60
Total nitrogen (%)	1.60	0.76	0.42
C/N ($mol\ mol^{-1}$)	14.80	9.91	8.52

Values for the lake bottom (1400 m) were extrapolated from the curve fittings shown in Fig. 2 (see also Table 4).
[a] Müller et al., 2005-this volume.

ophyceae, Chlorophyta and cyanobacterial picoplankton to the total chlorophyll *a* (Chl*a*):

$$\mathrm{Chl}a = 1.92^{*}(\mathrm{Fuco}) + 3.90^{*}(\mathrm{Chl}b) + 0.59^{*}(\mathrm{Zea}^{*}). \quad (1)$$

Those factors—given here in (mol Chl*a* mol^{-1} marker pigment)—were based on a data set comprising 89 water samples collected during a cruise in July 2001 in Lake Baikal. The factors were calculated by multiple linear regression and verified using CHEMTAX matrix factorisation software. Zea* means the cyanobacterial zeaxanthin calculated as difference between the total zeaxanthin and the small amount of zeaxanthin (less than 6% of total zeaxanthin) belonging to the Chlorophyta. This chlorophyta zeaxanthin was calculated from lutein using a zeaxanthin/lutein ratio of 5.3% (Nicklisch and Woitke, 1999).

According to this approach, the chlorophyll *a* content in the water of the south basin in July 2001 was composed by 30% Bacillariophyceae plus Chrysophyceae, 44% Chlorophyta, and 26% cyanobacterial picoplankton.

3.3. Pigments in the sediment traps

During 16 months of deployment, 239 g m^{-2} dry matter settled in the 40-m trap, with an average flux of 14.9 g m^{-2} $month^{-1}$ (Table 2 and Fig. 2). The content of organic carbon was 21.9% at that depth and that of total nitrogen 1.6% (Table 2 and Fig. 2). The resulting atomic C/N ratio of 15 indicated that the sedimented material resulted from the autochthonous production by suspended phytoplankton and that terrigenous input is likely to be negligible at that site. The amount of pigments gathered during the 16 months deployment in the 40-m trap was 193.1 μmol m^{-2} for chlorophyll *a* and 797 μmol m^{-2} for chlorophyllide *a*+pheopigment *a*. The average flux was hence 61.8 μmol m^{-2} $month^{-1}$ settled chlorophyll *a*+chlorophyllide *a*+pheopigment *a* (Table 1). It is worth noting that the replicate samples of the 40-m trap deviated strongly (coefficient of variation: 60.5%), whereas the coefficients of variation for the replicate samples in

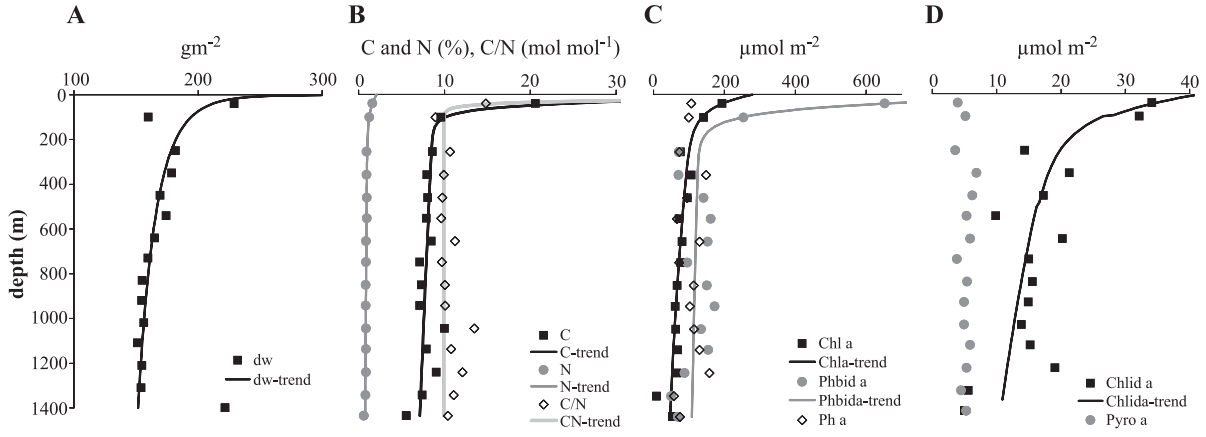

Fig. 2. Vertical profiles of settling particles in the water column, showing total mass fluxes (dw, g m^{-2}), organic carbon (C%), total nitrogen (N%), and atomic C/N ratios as well as vertical profiles of chlorophyll *a* (Chl*a*), and its degradation products (μmol m^{-2}). The traps were deployed for about 16 months. The respective regression equation and its coefficient of determinations (r^2) are reported in Table 4. Abbreviations: Chlid*a*—chlorophyllid *a*, Phbid*a*—pheophorbide *a*, Ph*a*—pheophytin *a*, PyroPh*a*—pyropheophytin *a*.

Table 3
Ratios of chlorophyll *a* and its degradation products per organic carbon in the 40-m trap, at the lake bottom, and in the topmost sediment sample

	40-m trap	1400-m trap μmol g^{-1}	Core top
Chlorophyll *a*/carbon	4.1	4.38	0.41
Chlorophyllide *a*/carbon	1.14	1.14	–
Pheopheorbide *a*/carbon	9.87	9.87	1.42
Pheophytin *a*/carbon	2.25	8.12	0.76
Pyropheophytin *a*/carbon	0.08	0.42	0.48

Values for the lake bottom were extrapolated from the curve fittings (Table 6 and Fig. 4). Data for chlorophyllide *a*/carbon and pheophorbide *a*/carbon, which did not show significant depth trends, were calculated as averages of all traps.

the traps below varied from 2.5% to 15.5%. Pheophorbide *a* was the most prominent degradation product in the 40-m trap, while pheophytin *a*, pyropheophytin *a*, and chlorophyllide *a* occurred in much lower amounts (Table 1 and Fig. 2). With respect to organic carbon, however, only 3.9 μmol g^{-1} chlorophyll *a* but 9.47 μmol g^{-1} pheophorbide *a* were found (Table 3). The lowest ratio was found for pyropheophytin *a*/carbon (Table 3).

In the 40-m trap, fucoxanthin was the dominant carotenoid (Table 1 and Fig. 3). Other pigments of Bacillariophyceae plus Chrysophyceae (chlorophyll *c*, diadinoxanthin, and diatoxanthin) as well as the cyanobacterial zeaxanthin also showed high sedimentation rates, whereas the chlorophyte chlorophyll *b* and lutein, as well as the cryptophyte alloxanthin, sedimented only in low amounts (Table 1 and Fig. 3).

A PCA including the dry matter, organic carbon, and total nitrogen as well as all pigments revealed that three components controlled 90.7% of the variance. The first component (65.5%) included the depth and controlled dry matter, organic carbon and nitrogen. The first component controlled also the labile pigments chlorophylls *a*, *b*, and *c* as well as chlorophyllide *a* and pheophorbide *a* and also all carotenoids. The second and third components comprised the more stable pigments pheophytin *a*, pyropheophytin *a*, and pheophytin *b*. The sedimentation to the lake bottom showed a power regression for dry matter, but two-exponential or two first-order independent decay regressions were apparent for organic carbon, total nitrogen, chlorophylls *a*, *b*, *c*, chlorophyllide *a*, pheophorbide *a*, and most carotenoids (Tables 4 and 5, and Figs. 2 and 3). In contrast, for the more stable chlorophyll degradation products, pheophytin *a*, pyropheophytin *a*, and pheophytin *b*, none of those regression models fitted accurately (Fig. 2). The composite character of the regressions (Tables 4 and 5) indicated that the degradation passed through two different phases, triggered by different factors. The first degradation phase occurred within the upper 250 m and was much stronger than the second. Below

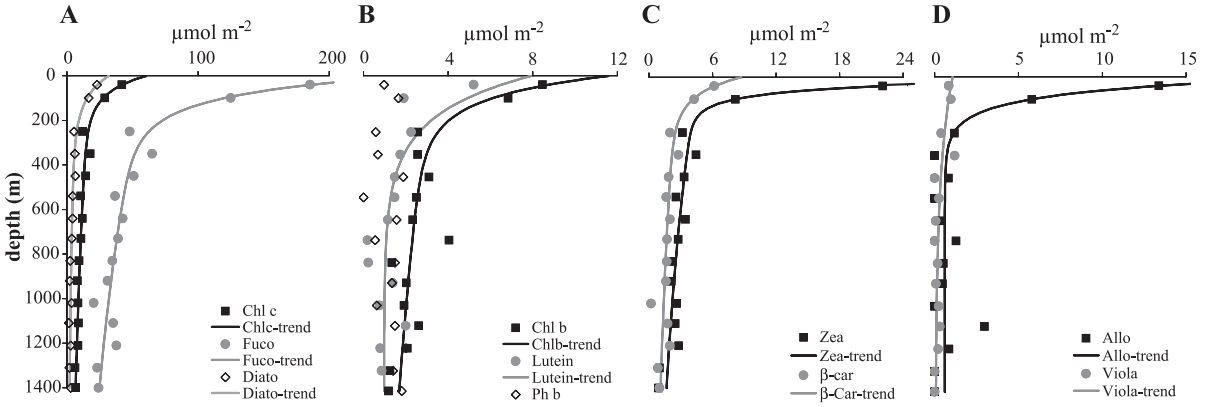

Fig. 3. Depth profiles of marker pigments from Bacillariophyceae plus Chrysophyceae (A), Chlorophyta (B), cyanobacterial picoplankton (C), Eustigmatophyceae, and Cryptophyta (D). The traps were deployed for about 16 months. The respective regression equations and its coefficients of determination (r^2) are reported in Table 5. Abbreviations: Chl—chlorophyll, Fuco—fucoxanthin, Zea—zeaxanthin, β-car—β-carotene, Allo—alloxanthin, Viola—violaxanthin.

Table 4
Power ($y=ax^b$) and two first-order independent decay ($y=a*\exp^{(-bx)}+c*\exp^{(-dx)}$) models of the decrease in the dry matter (y=g m^{-2}) as well as of the organic carbon and total nitrogen percentages (y=%) and the C/N ratio (y=mol mol^{-1})

	Function (y=)	Factors				r^2	P
		a	b	c	d		
Dry weight	$a*x^b$	299.7	–0.094	–	–	0.691	<0.01
P		<0.01	<0.01				
Organic carbon	$a*\exp^{(-bx)}+c*\exp^{(-dx)}$	76.24	0.044	8.8	$1.5\ 10^{-4}$	0.921	<0.01
P		0.335	0.111	<0.01	0.238		
Total nitrogen	$a*\exp^{(-bx)}+c*\exp^{(-dx)}$	1.09	0.016	1.03	2.210^{-4}	0.945	<0.01
P		<0.01	<0.05	<0.01	<0.01		
C/N	$a*\exp^{(-bx)}+c*\exp^{(-dx)}$	223.26	0.09	9.91	$1\ 10^{-12}$	0.496	0.05
P		0.982	0.937	<0.01	1.00		

x designates the depth in (m), r^2 the respective squared correlation coefficient, and P the significance.

250–300 m, the degradation became visibly lowered. Calculations of simple exponential or decay models for those pigments resulted in much lower coefficients of determinations or insignificant models. Therefore, one simple phase cannot describe the pigment degradation with depth.

The functions given in Tables 4 and 5 should allow reconstructions of initially settled pigments from trap or sediment data in further investigations. The models are nevertheless preliminary, as they do not take into account different degradation extents within the traps.

Table 5
Single exponential ($y=a+b*\exp^{(-x/c)}$), two exponential ($y=a*\exp^{(-x/b)}+c*\exp^{(-x/d)}$), two first-order independent decay ($y=a*\exp^{(-bx)}+c*\exp^{(-dx)}$) models of the decrease of the distinct pigments

	Function (y=)	Factors				r^2	P
		a	b	c	d		
Chlorophyll *a*	$a*\exp^{(-x/b)}+c*\exp^{(-x/d)}$	115.71	1527.48	166.54	56.02	0.873	<0.01
P		<0.01	<0.01	0.082	0.187		
Pheophorbide *a*	$a*\exp^{(-x/b)}+c*\exp^{(-x/d)}$	129.75	7580.95	1399.42	40.75	0.926	<0.01
P		<0.01	0.673	<0.01	<0.01		
Chlorophyllide *a*	$a*\exp^{(-x/b)}+c*\exp^{(-x/d)}$	20.71	2184.81	22.74	101.19	0.717	<0.01
P		<0.05	0.242	0.082	0.417		
Chlorophyll *c*	$a*\exp^{(-x/b)}+c*\exp^{(-x/d)}$	17.5	1446.95	43.38	74.46	0.969	<0.01
P		<0.01	<0.01	<0.01	<0.01		
Fucoxanthin	$a*\exp^{(-x/b)}+c*\exp^{(-x/d)}$	60.39	1574.39	204.84	85.37	0.973	<0.01
P		<0.01	<0.05	<0.01	<0.05		
Diatoxanthin	$a*\exp^{(-x/b)}+c*\exp^{(-x/d)}$	6.69	1179.54	25.39	99.04	0.976	<0.01
P		<0.01	<0.05	<0.01	<0.01		
Alloxanthin	$a+b*\exp^{(-x/c)}$	0.603	23.53	65.69	–	0.953	<0.01
P		<0.05	<0.01	<0.01			
Chlorophyll *b*	$a*\exp^{(-x/b)}+c*\exp^{(-x/d)})$	3.23	2160.57	8.42	96.91	0.886	<0.01
P		<0.01	0.24	<0.01	0.080		
Lutein	$a+b*\exp^{(-x/c)}$	0.969	6.99	173.73	–	0.916	<0.01
P		<0.01	<0.01	<0.01			
Violaxanthin	$a+b*\exp^{(-x/c)}$	0.04	1.03	392.24	–	0.555	<0.01
P		0.842	<0.01	0.193			
Zeaxanthin	$a*\exp^{(-x/b)}+c*\exp^{(-x/d)}$	4.64	1358.65	48.89	39.11	0.988	<0.01
P		<0.01	<0.01	<0.01	<0.01		
β-carotene	$a*\exp^{(-x/b)}+c*\exp^{(-x/d)}$	2.63	1592.24	6.15	76.93	0.895	<0.01
P		<0.01	0.075	<0.01	0.082		

y designate the pigment content in (μmol m^{-2}), x the depth in (m), r^2 the respective squared correlation coefficient, and P the significance.

Different degradation patterns were revealed when chlorophylls and its degradation products were referred to organic carbon (Fig. 4) instead of area references (Fig. 2). Fig. 4 visualises differences in the degradation between the organic compounds, chlorophylls, and carbon. The chlorophyll *a*/carbon ratio decreased with depth, indicating that organic carbon is more slowly degraded than chlorophyll *a* (Table 6 and Fig. 4), whereas the pheophytin *a*/carbon ratio and the pyropheophytin *a*/carbon ratio increased with the depth, indicating the formation of pheophytin and pyropheophytin with depth (Table 6 and Fig. 4). Best fits for the chlorophyllide *a*/carbon ratio and pheophorbide *a*/carbon ratio vs. depth were also linear regression models, but they were not significant (Fig. 4).

Considering that the 40-m trap was collecting 100% of the particles that settled out of the euphotic zone, 100% dry matter would be 14.9 mg m^{-2} $month^{-1}$ (Table 2). At 100 m, 10 mg m^{-2} $month^{-1}$ dry matter were collected which accounts for 67%. At the lake bottom, an estimate of 64% of dry matter settled down. The estimated percentages of organic carbon and total nitrogen, which reached the lake bottom, were, in contrast, only 33% and 48%, respectively (Table 2 and Fig. 2). The organic compounds were obviously more strongly degraded than the nonorganic fraction (mainly siliceous valves of diatoms) of the settled material. The loss during the sedimentation was, however, even stronger for most of the pigments. Only 24% of chlorophyll *a* reached the lake bottom and 21% of chlorophyll *b* (Table 1 and Fig. 3). The distinct degradation products of chlorophyll *a* showed different losses. About 100% of the pheophytin *a* reached the lake bottom, but only 16% of pheophorbide *a*. For the comparison of the fluxes in the traps with the standing crop in the euphotic zone, chlorophyll *a* concentrations of the July phytoplankton community (2001) were available. The estimated amount of chlorophyll *a*, integrated over 40-m water column, was 66 µmol m^{-2} (Table 1). Assuming that amount represents a mean value over the 16 months of deployment, the ratio between standing crop and chlorophyll *a*+chlorophyllide *a*+pheopigment *a* flux per month at 40 m was 0.94 and at the lake bottom was 0.26.

According to the contribution to the chlorophyll *a*-model shown in Eq. (1), the chlorophyll *a* content in the water of the south basin in July 2001 was

Table 6
Linear regressions for the chlorophyll *a*/carbon, pheophytin *a*/carbon, and pyropheophytin *a*/carbon ratios vs. depth (*y*=µmol g^{-1})

	Function (*y*=)	Factors		r^2	*P*
		a	*b*		
Chlorophyll *a*/carbon	*a*+*bx*	7.18	−0.002	0.301	<0.05
P		<0.01	<0.05		
Pheophytin *a*/carbon	*a*+*b*/*x*	8.29	−241.4	0.327	<0.05
P		<0.01	<0.05		
Pyropheophytin *a*/carbon	*a*+*b*/*x*	0.429	−13.5	0.614	<0.01
P		<0.01	<0.01		

x designates the depth in (m), r^2 the respective squared correlation coefficient, and *P* the significance.

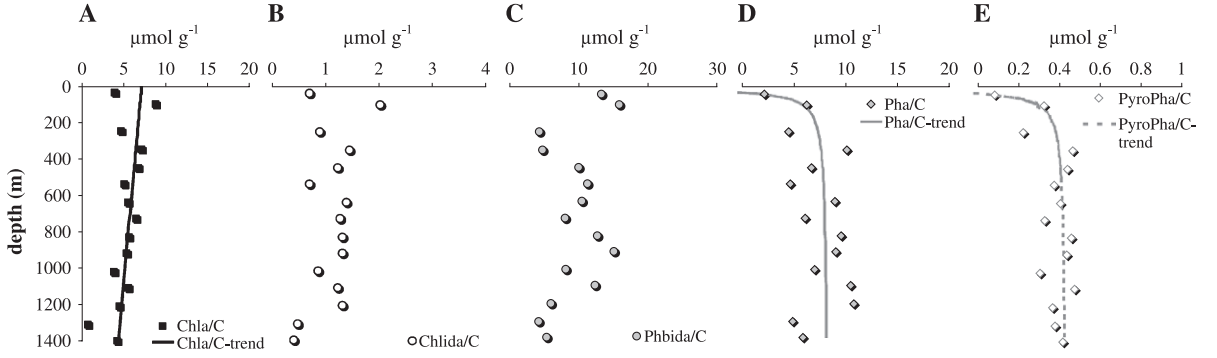

Fig. 4. Depth profiles of chlorophyll *a*/carbon ratio (Chl*a*/C), chlorophyllide *a*/carbon ratio (Chlid*a*/C), pheophorbide *a*/carbon ratio (Phbid*a*/C), pheophytin *a*/carbon ratio (Ph*a*/C), and pyropheophytin *a*/carbon ratio (PyroPh*a*/C). The respective regression equations and its coefficient of determination (r^2) are reported in Table 6.

composed of 30% Bacillariophyceae plus Chrysophyceae, 44% Chlorophyta, and 26% cyanobacterial picoplankton. In the 40-m trap, in contrast, 87% of the chlorophyll *a* originated from Bacillariophyceae plus Chrysophyceae, 11% from Chlorophyta, and 2% from cyanobacterial picoplankton (Fig. 5). The percentage contribution did not change with the water depth, as the same composition was found in the deepest traps (Fig. 5).

In all traps, the calculated chlorophyll *a* concentration—based on the marker pigments, as shown in Eq. (1)—was much higher compared to the measured chlorophyll *a* concentration. On average, the calculated value of the chlorophyll *a* concentration was 157% of the measured value. Pheopigment *a*, which results from grazing and photooxidation, were not added to chlorophyll *a* because carotenoid degradation products, resulting from the same processes, were also not added to the marker pigments. Adding chlorophyllide *a*, that occurs in senescent cells due to enzymatic lyses, which does not affect carotenoids

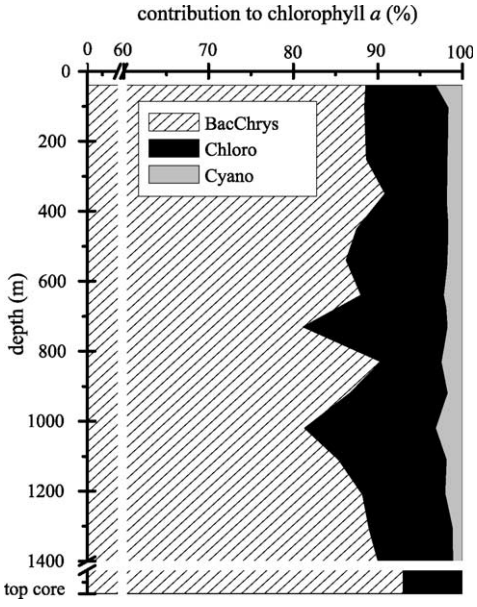

Fig. 5. Depth profiles of the contribution to total chlorophyll *a*+chlorophyllide *a* by Bacillariophyceae plus Chrysophyceae (BacChrys), Chlorophyta (Chloro), and cyanobacterial picoplankton (Cyano). Calculations were based on factors established for 89 water samples across Lake Baikal in July 2001 (see text). The traps were deployed for about 16 months and the core top spanned c. 7 years (see text).

(Jeffrey et al., 1997), the mean calculated chlorophyll *a*+chlorophyllide *a* concentration was 121% the measured value. This overestimation could result from an unusual high carotenoid or chlorophyll *b*/chlorophyll *a* ratio of specific settling taxa or from a higher degradation rate of chlorophyll *a* than carotenoids or chlorophyll *b*. The second assumption is likely.

A conclusion concerning the source of pheopigment *a*, as has been shown for chlorophyll *a*, is limited, because marker pigments which underwent a similar degradation then pheopigments are missed. The only share which can be calculated is for Chlorophyta assuming that the ratio of pheophytin *a* to pheophytin *b* represents the former ratio of chlorophyll *a* to chlorophyll *b* in the settling material. Then, the factor given in Eq. (1) for the chlorophyll *a*/chlorophyll *b* relationship can be adopted for the pheophytin *a*/pheophytin *b* relationship. According to this approach, 2.6% of pheophytin *a* should originate from Chlorophyta.

3.4. Pigments in the surface sediment

According to ^{210}Pb-dating, the accumulation rate of dry matter in the core top was 89 g m^{-2} yr^{-1}, hence giving an average of 7.41 g m^{-2} month^{-1} (Table 2). The amount of dry matter diminished only slightly between the deep hypolimnion water (trap) and the surface sediment (22%, Table 2), but the percentage of organic carbon (52%) and total nitrogen (45%) diminished to a greater extent (Table 2). As the C/N ratio was similar to that found in traps, the source of the organic matter of the surface sediment seems to be predominantly autochthonous like the material of the traps. The trap material in almost all traps was thought to be anoxic because of the dark grey colour, dead *Gammarus*, the smell of hydrogen sulphide (H_2S) and a lack of oxidised ferric iron (Fe(III)), whereas the topmost centimetre of the surface sediment was oxic (Müller et al., 2005-this volume). High degradation could therefore be expected.

Chlorophyll *a*, pheophorbide *a*, and pheophytin *a* showed strong decreases between the hypolimnion water and the surface sediment, whereas the decrease of the pyropheophytin *a* amount was much weaker (Table 1). Referred to organic carbon, the stability of pyropheophytin *a* was more obvious since the

pyropheophytin *a*/carbon ratio even increased in the surface sediment compared to the lake bottom, whereas all other chlorophylls and degradation products vs. carbon ratios decreased to less than 20% (Table 3). Besides being more stable, pyropheophytin *a* was probably also formed by processes after burial. However, that in the surface sediment intact chlorophyll *a* has even been found, marked the importance of the sedimentation of living or at least moribund cells. Other stable products after burial were pheophytin *b*, which was found at 56% and chlorophyll *b* which was found at 25% compared to the deepest traps (Table 1). The detected carotenoids showed losses of up to 95% (Table 1).

Only 1.2% of the settled crop were finally deposited, assuming the determined estimate of 61.8 μmol m^{-2} $month^{-1}$ chlorophyll *a*+chlorophyllide *a*+pheopigment *a* as a flux below the euphotic zone (Table 1). According to the contribution to chlorophyll *a*-model, as has been shown for the euphotic zone as well as for the sediment traps (Eq. (1)), 93% of the surface sediment pigments resulted from Bacillariophyceae plus Chrysophyceae and 7% from Chlorophyta (Fig. 5). Marker pigments from cyanobacterial picoplankton were not detected. That marks a clear shift towards fucoxanthin-containing Bacillariophyceae plus Chrysophyceae and chlorophyll *b*-containing Chlorophyta at the expense of cyanobacterial picoplankton (Table 1).

4. Discussion

The aim of this study was to determine preliminary transfer functions for the organic matter, especially lipophilic photosynthetic pigments, and to infer how the main phytoplankton groups were represented in the deposited material. The mass fluxes of dry matter as well as of chlorophyll *a*, pheopigment *a*, and carotenoids in Lake Baikal correspond well to those found in different oceanic regions (Welschmeyer and Lorenzen, 1985a,b; Landry et al., 1995; Barlow et al., 1995; Nodder and Gall, 1998). Fluxes in the moderately productive marine Dabob Bay, in contrast, were much higher (Welschmeyer and Lorenzen, 1985a). Due to its extreme depth and extension of the euphotic zone, organic matter fluxes in Lake Baikal should be compared with marine rather than with freshwater systems. Mass and pigment fluxes correspond also to different oligo- to mesotrophic lakes, whereas eutrophic lakes showed higher rates, but the depths of those lakes varied from 3 to 36 m only (Hurley and Armstrong, 1991; Baines and Pace, 1994; Poister et al., 1999). Pigment degradation processes in deep lakes are poorly known.

Another peculiarity of Lake Baikal, which brings Lake Baikal closer to oceanic systems, is the permanent temperature of 3–4 °C below 250 m and the higher temperatures of 12–15 °C during summer stratification in the epilimnion (Kozhova and Izmest'eva, 1998). The low temperatures might depress the degradation rates relative to shallower and warmer aquatic systems because most degradation processes (photooxidation, grazing, etc.) are temperature dependent (Leavitt, 1993). On the other hand, Lake Baikal is oxygenated down to the maximal depth due to lake overturn, convections, and deep-water currents (Weiss, 1991), and enhanced oxidation might occur across the whole water column.

In Lake Baikal, the most prominent degradation of the settling material occurs within the upper 250 m water column, which is the wind-mixed depth during overturn, where particles are suspended (Müller et al., 2005-this volume). The degradation below 250 m was very low for most pigments. The biphasic character of the flux curves (Tables 3 and 4, and Figs. 2 and 3) clearly highlights that the degradation is divided into a stronger and weaker degradation phases. Only 24% of the trapped chlorophyll *a* at 40 m settled deeper than 250 m. These low rates indicated that the initially settling chlorophyll *a* was transformed into pheopigments or colourless compounds. Possible causes could be (i) photooxidation due to extended residence in the euphotic zone during mixing, (ii) death of living or moribund settling cells in the dark during stratification, or (iii) zooplankton grazing and further bacterial destruction.

Photooxidation due to extended residence in the euphotic zone by wind induced turbulence, might explain the losses between the suspended and the settled matter, but it can only affect the uppermost trap, as the euphotic zone is limited to approximately 40 m (Kozhova and Izmest'eva, 1998). Thus, the loss of chlorophyll *a* between 40 and 250 m should be caused by the death of settling cells in the dark or

grazing. The loss of chlorophyllide *a* (which may represent moribund cells) may be caused by autolysis, bacterial destruction, or by grazing. The much stronger decrease of pheophorbide *a* between 40 and 250 m almost certainly results from mesozooplankton faecal pellets being destroyed.

Death of living or moribund cells in the dark might be less common in Lake Baikal than in other aquatic systems. For the Dabob Bay and Central Pacific Gyres (Welschmeyer and Lorenzen, 1985a,b), as well as for a marine convergence zone (Head and Horne, 1993), an over tenfold higher average of pheopigment *a* than chlorophyll *a* flux was found. As chlorophyll *a* is associated to the flux of intact cells, sinking of intact cells is an insignificant loss term in those areas. In Lake Baikal, in contrast, the pheopigment *a* flux was only three times the chlorophyll *a* flux, and it can therefore be assumed that sinking of living cells is important. Furthermore, chlorophyllide *a*, which is formed by enzymatic activity after cell death, occurred only at a ratio of 0.2 chlorophyllide *a*/chlorophyll *a* (Table 1), while in Lake Mendota, sediment traps ratios of 0.7 were found (Hurley and Armstrong, 1990). The importance of the sinking of living cells can be explained by the high inherent sinking rates of "heavy" Bacillariophyceae as bacillariophycean sinking rates of 60–100 m day^{-1} have been reported in Lake Baikal (Ryves et al., 2003).

Pigment destruction by zooplankton grazing is a complex issue: rates of transformation and degradation depend on gut passage time, and hence of edible cell concentration and even on food quality. It has been shown that micro-and mesozooplankton can degrade chlorophyll *a* in part or even entirely into nonfluorescent breakdown products (Klein et al., 1986; Burkill et al., 1987; Barlow et al., 1988; Head and Harris, 1992). The extent of the degradation depends also from the grazer size (Carpenter and Berquist, 1985; Carpenter et al., 1988). Small protozoa, for example, degrade more efficiently compared to large protozoa (Strom et al., 1998). On the other hand, grazer size implies differences of faecal packaging and sinking rates. Faecal pellets of mesozooplankton, such as cladocerans, have high sinking rates, whereas faecal debris of microzooplankton, such as protozoa, have negligible sinking rates (Welschmeyer and Lorenzen, 1985a). High sinking rates tend to prevent photooxidation, while low sinking rates lead to long permanence within the euphotic zone and therefore to a conversion into colourless products. Pheopigments found in the traps may originate from mesozooplankton rather than from microzooplankton since they were found in the traps but not in the water samples, and hence they may originate from fast-sinking faecal pellets (Welschmeyer and Lorenzen, 1985a).

An uncertainty results from the fact that traps were deployed for a period of 16 months, as internal degradation processes that occurred after the cells have settled down could not be determined. In marine environments, pheopigment *a* degradation by senescence and dark degradation are negligible processes (Welschmeyer and Lorenzen, 1985a). In addition, the traps were anoxic, limiting therefore most degradation processes. It can therefore be assumed that the biggest part of degradation occurred before the settlement into the traps.

Another extensive degradation before permanent burial occurred at the sediment surface. Most pigments occurred in much lower concentrations in the core top, than even in the deepest sediment traps. Cuddington and Leavitt (1999) predicted that rates of pigment deposition were inversely related to the thickness of the oxic zone. The oxygen penetration into the sediment reached 2 cm (Martin et al., 1993; Müller et al., 2005-this volume), whereas the anoxic sediment trap material in contrast remained relatively protected from oxidation after burial into the traps. Only 3.8% of the chlorophyll *a* that reached the lake bottom was preserved in the surface sediment (Table 1). Therefore, living or moribund cells diminished strongly within the water to sediment interface. The preservation of pheophorbide *a* and also of pheophytin *a* was similar to that of chlorophyll *a*. Pyropheophytin *a*, in contrast, was preserved at 39%. A conversion from pheophytin *a* to pyropheophytin *a*, where pheophytin *a* loses its methylcarboxylated group, could also be possible (Jeffrey et al., 1997). The degradation of chlorophyll, pheophorbid, and pheophytin was much stronger than that of organic carbon. Typical chlorophyll *a*/carbon ratios in phytoplankton are 6–28 μmol g^{-1} (Sterner and Elser, 2002), and whereas the chlorophyll *a*+pheopigment *a* vs. carbon ratios found in the traps were within that range, the ratios found in the surface

sediment were much lower (3 μmol g^{-1}; Table 3). These low ratios within the sediment surface follow from the deep oxygen penetration (Martin et al., 1993; Müller et al., 2005-this volume).

Some studies indicated that fossil pigment concentration directly reflects the standing crop abundance in the euphotic zone, while others indicated that up to 99% of the autochthonous pigments are lost during sinking (see review in Leavitt, 1993). In this first study, we present a loss of about 72% during sinking but up to 99% loss before the permanent burial. Similar high losses were found for the major lipid biomarker classes (Russell and Rosell-Melé, 2005-this volume); thus, the figures here are likely to be a reliable dimension for the losses in a deep oxygenated lake. Cuddington and Leavitt (1999) concluded from their theoretical model that historical correlations between phytoplankton production and pigment deposition should be strongest when lake morphometry and oxygen and light penetration are relatively constant. The validity of this assumption for the investigated and other sites within Lake Baikal has to be proven by comparing long-term monitoring data of the standing crop with surface sediment slices in future studies.

The relative contribution of the various accessory pigments can be used to infer various algal groups as sources of sinking material. The contributions of dominant phytoplankton groups could be determined with appropriate factors for the respective marker pigments (see Eq. (1); Fietz and Nicklisch, 2004). However, these calculations showed several limits when applied to the traps.

On the one hand, the total chlorophyll *a* concentrations in the sediment traps could not be accurately estimated based on the factors determined for the water samples. It has been suggested that the overestimation of chlorophyll *a* resulted from a stronger degradation of carotenoids or chlorophyll *b* than chlorophyll *a*. Carotenoids are more stable than chlorophylls in the presence of light and oxygen (Leavitt and Findlay, 1994) and in the presence of grazers (Strom et al., 1998), but in oxic surface sediments of Lake Baikal, carotenoids were more susceptible to decomposition than chlorophylls (Soma et al., 2001). Further, fucoxanthin—the predominant carotenoid—easily decomposes and only zeaxanthin—which contributes only a small amount to the total chlorophyll *a*—is known to be stable (Leavitt and Findlay, 1994). The differential chlorophyll and carotenoid degradations might therefore not be applied from one aquatic system to another.

On the other hand, based on the factors shown in Eq. (1), Bacillariophyceae plus Chrysophyceae dominated the sinking material at 90% and Chlorophyta and cyanobacterial picoplankton made only minor contributions. The calculation for the summer standing crop indicated that Chlorophyta contributed a higher part than Bacillariophyceae plus Chrysophyceae and that the cyanobacterial picoplankton contributed c. 26%. Hence, the record of the phytoplankton standing crop by trapped pigments in Lake Baikal was group-specific. Some carotenoids are more preserved than others, and they cannot record whole algal assemblages, unlike differential degradation rates be taken into account. This has been found also for several shallow lakes in surface sediment studies (Leavitt and Carpenter, 1990; Leavitt, 1993; Leavitt and Findlay, 1994). The estimates of the differential degradation rates presented here for Lake Baikal (Table 5) may improve further reconstructions of the phytoplankton composition.

The pigment- or group-specific sedimentation might be caused by two factors: first, water samples were taken only in July, when summer begins in Lake Baikal. Then, cyanobacteria and Chlorophyta usually contribute a higher part to the community than during spring and winter (Kozhova and Izmest'eva, 1998; Popovskaya, 2000). Over all, two spring Bacillariophyceae peaks were recorded within the 16 months of deployment (M. Sturm, unpublished results from sequencing traps). Nonetheless, a dominance of 90% is not common during most of the year and hence, even the rough comparison with long-term studies (Kozhova and Izmest'eva, 1998; Popovskaya, 2000), indicate that a 90% dominance of Bacillariophyceae plus Chrysophyceae marks a group-specific sedimentation. Second, fucoxanthin in Lake Baikal originated sometimes from very large Bacillariophyceae (Fietz and Nicklisch, 2004) which have very fast sinking rates (60–100 m day^{-1}, Ryves et al., 2003) so that pigments, including the bacillariophycean part of chlorophyll *a*, suffered less from light induced degradation processes than pigments of the smaller Chlorophyta and the cyanobacterial picoplankton. Selective grazing might also be an important factor,

as it can also be assumed that autotrophic picoplankton is preferentially grazed by microzooplankton and mesozooplankton, whereas large siliceous Bacillariophyceae suffered less from zooplankton grazing (Hurley and Armstrong, 1990). Similar problems are well known from established methods such as bacillariophycean valve-based analyses. Battarbee et al. (2005-this volume) also warn that differential dissolution of diatom species occurs mainly at the surface sediment–water interface.

In Lake Baikal, the main contribution to the settling material was in this study formed by heavy, nonedible Bacillariophyceae. Strong and variable degradation processes control the sedimentation of small, light, and edible phytoplankton. Basically, these processes take place within the upper 250 m of the water column and a second degradation based on different factors takes place within the oxygenated surface sediment. The sedimentation out of the euphotic zone can be projected backward using the preliminary regression models given in the present study.

In as much as the palaeoecological analysis of preserved markers such as photosynthetic pigments is increasingly used to monitor environmental change in response to climate and human activities, the complexity and variability of the degradation, revealed in this first study, should improve our understanding of the limits of such retrospective analyses. Because Lake Baikal is unusual in terms of size and depth, it represents an interesting end-member in investigations of pigment biogeochemistry. The conclusions are difficult to apply to other mainly shallower freshwater systems, but can considerably contribute to the understanding on the manner in which organic molecules are incorporated into the sediments in cold, deep, oxygenated lakes and in marine systems.

Acknowledgments

Thanks are due to Michael Schurter and Alois Zwyssig (EAWAG, Switzerland) and to the captain and crew of the Research Vessel “Vereshchagin” for the successful deployment and recovery of the mooring. We wish also to thank two anonymous reviewers and A.W. Mackay for constructive objections and improvement of the manuscript. We acknowledge H. Oberhänsli for the organisation and permanent support of the CONTINENT project. This study has been funded by the EU-project CONTINENT, Contract no. EVK2-2000-00057.

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