

# Multi-proxy reconstruction of trophic state, hypolimnetic anoxia and phototrophic sulphur bacteria abundance in a dimictic lake in Northern Germany over the past 80 years

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**Abstract** During monthly investigations from 1996 to 2000, a hypolimnetic layer of phototrophic sulphur bacteria (*Chromatium* spp.) were observed in Lake Dudinghausen, a small dimictic lake in northern Germany. This paleolimnological study was initiated to detect if the occurrence of sulphur bacteria was related to cultural eutrophication or reflected natural conditions. Therefore, diatoms, algal pigments, okenone, geochemical proxies, and  $^{210}\text{Pb}$  and  $^{137}\text{Cs}$  were used in four sediment cores to investigate historical changes in trophic development, hypolimnetic redox conditions, anoxia and phototrophic sulphur bacteria abundances. Fossil diatoms, pigments, the ratio of chlorophyll derivatives to total carotenoids and the ratio of chlorophyll *a* to its derivatives suggest two phases of eutrophica-

tion coupled with hypolimnetic anoxia over the last ~80 years: a first phase from about 1923–1932 and a second from 1952 to 1982. In the first phase the ratios of Fe–Mn as well as Fe–Ca increased, suggesting seasonal anoxia. However, hypolimnetic anoxia was only weak because low levels of okenone suggest no mass development of sulphur bacteria. In contrast, sulphur bacteria increased during the early stages of the second eutrophication phase, suggesting increased temporal and spatial hypolimnetic anoxia. Surprisingly, the ratios of Fe–Mn as well as Fe–Ca decreased during this time. Possibly Fe, Mn and Ca were equally reduced through the intense anoxia. In the final stage, sulphur bacteria decreased again. As these bacteria need both anoxic conditions and a certain amount of light, the increased nutrient load probably led to low Secchi depth and therefore insufficient light conditions. In more recent years, diatoms and pigments suggest a decrease in nutrient levels. A second mass development of sulphur bacteria occurred, probably due to improved light conditions and continued anoxia in the upper hypolimnion. We conclude that the recent development of phototrophic sulphur bacteria do not represent natural conditions in Lake Dudinghausen. Furthermore, the upper sediments contain a completely new diatom flora that never occurred in older sediments of Lake Dudinghausen. Therefore, nutrient levels may eventually reach natural conditions, however

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they may not represent biological background reference conditions.

**Keywords** Trophic state · Anoxia · Diatoms · Fossil algal pigments · Okenone · Metal ratios · Lake development · Natural background conditions

## Introduction

Eutrophication is a major factor of past and recent lake developments, and also the major problem for water conservation for lowland lakes in northern Germany (Scharf 1998; Schönfelder et al. 2002; Mathes et al. 2003). Increasing nutrient levels in lakes are characterised by higher primary production and changing algal communities (Wetzel 1970; Reynolds 1998; Waters et al. 2005). Additionally, the higher nutrient load leads to increased sedimentation rates, increased spatial and temporal hypolimnetic anoxia and changes in hypolimnetic redox conditions (Mortimer 1941; Kampf-Nielsen 1974). Amongst other changes, the occurrence of sulphur bacteria often indicates a higher eutrophication state of a lake, as these bacteria require, for example, anoxic hypolimnetic conditions (Züllig 1986).

The reconstruction of natural lake conditions (reference conditions) are crucial for management strategies and restoration concepts (Battarbee 1999). To infer past nutrient levels, several robust and well established paleolimnological indicators are commonly used, for example diatoms (Bennion and Appleby 1999; Köster et al. 2004; Miettinen et al. 2005; Reid 2005; Werner and Smol 2005), fossil algal pigments (Sanger and Gorham 1972; Overmann et al. 1993; Feuillade et al. 1995; Guilizzoni et al. 1996; Waters et al. 2005), okenone (pigments of phototrophic sulphur bacteria) (Züllig 1986), geochemical sediment parameters (Bengston and Persson 1978; Rippey 1990) and metals such as Fe and Mn (Garrison and Wakeman 2000).

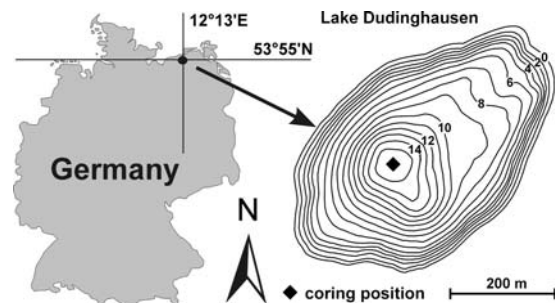
Lake Dudinghausen, the study lake used in this investigation, is a typical, dimictic lowland lake in northern Germany. During summer stratification phosphorus is released from surface

sediments due to an anoxic hypolimnion (Selig and Schlungbaum 2003). Also, in addition to the epilimnetic phytoplankton community, a second layer of primary production with phototrophic sulphur bacteria was observed in the hypolimnion from 1996 to 2001 (Selig et al. 2004). These recent investigations revealed no information about the lakes' trophic development in the past and, therefore, could not identify if a restoration of the lake is possible or/and necessary.

The aim of this study is therefore to answer the following key question: Is the recent occurrence of phototrophic sulphur bacteria in the hypolimnion of Lake Dudinghausen an episode related to increased cultural eutrophication or does it reflect natural conditions? Therefore, we reconstructed the historical trophic development of Lake Dudinghausen using diatoms, algal pigments, okenone, geochemical parameters and metals to infer: (1) the nutrient levels in the lake, (2) the redox conditions on the sediment-water interface and anoxia in the hypolimnion, and (3) the relationship between trophic state and redox conditions in this lake.

## Study site

Lake Dudinghausen (53°55' N, 12°13' E) is situated 22.4 m above sea level in Mecklenburg–Western Pomerania, northeast Germany (Fig. 1). The lake is of glacial origin and its catchment area comprises 0.25 km<sup>2</sup>. The lake is dimictic, holomictic and meso- to eutrophic, and has an anoxic hypolimnion with phosphorus release from the



**Fig. 1** Geographical position, bathymetric map and core sampling site (15.2 m water depth) of Lake Dudinghausen. Depth intervals are in meters

surface sediment during summer stratification (Selig and Schlungbaum 2003; Selig et al. 2004). Further limnological details are shown in Table 1. The recent epilimnetic phytoplankton biomass reached annual peaks of  $5.83 \text{ mm}^3 \text{ l}^{-1}$  (1997),  $23.65 \text{ mm}^3 \text{ l}^{-1}$  (1998) and  $6.25 \text{ mm}^3 \text{ l}^{-1}$  (1999). The phytoplankton is characterised by diatoms (spring: *Stephanodiscus minutulus* (Kützing) Cleve & Möller; autumn: *Cyclotella ocellata* Pantocsek, *Cyclotella krammeri* Håkansson), diverse coccal chlorophytes (pre-summer) and cyanobacteria (late-summer: *Aphanizomenon flos-aque* Ralfs, *Microcystis aeruginosa* (Kützing) Kützing). Macrophytes are relatively unimportant and only rarely distributed along a small strip near the shoreline in Lake Dudinghausen. Phototrophic sulphur bacteria were found in the upper part of the hypolimnion from August to October (1996–2001). The bacteriochlorophyll *a* concentration varied from 12 to  $36 \mu\text{g l}^{-1}$ . The biomass maximum is  $7.6 \text{ mm}^3 \text{ l}^{-1}$ , dominated by *Chromatium* spp. (Selig et al. 2004).

## Material and methods

### Sediment coring and sub-sampling

The sediment material used in this study was derived from four short sediment cores (DUD KK 2000) (length of 56, 55, 52 and 43 cm) taken in May 2000. The cores were retrieved from the same site using a Mondsee corer (UWITEC,

Austria) at 15.2 m water depth (for core locations see Fig. 1). For sub-sampling, the sediment was divided into 1 cm sections for the chemical sediment parameters (55 cm core) and for the age determination (56 cm core). For analyses of diatoms (52 cm core), samples were taken in intervals of 2 cm. Samples for pigment analyses were taken from the 43 cm core at 1 cm intervals except at 25, 30 and 36 cm depth. Correlation between cores was checked using characteristic diatom assemblages of certain depths. The core depths between cores differ at the most one or two cm.

### Chronology

The chronology analysis of the freeze-dried sediment was done at the Leibniz Laboratory for Radiometric Research at the University of Kiel. Radionuclides  $^{210}\text{Pb}$  and  $^{137}\text{Cs}$  activities were measured using a germanium-semiconductor-detector-system for a minimum of 48 h based on gamma radiation of 46.5 kV and 661 kV (Appleby et al. 1992). The sediment core chronology was calculated using the Constant Rate of Supply (CRS) model (Appleby and Oldfield 1983).

### Diatom analyses

Samples for diatom analyses (ca.  $2 \text{ cm}^3$ ) were treated with HCl,  $\text{H}_2\text{O}_2$ ,  $\text{H}_2\text{SO}_4$ , and  $\text{KMnO}_4$  following Kalbe and Werner (1974). The distilled water-cleaned and air-dried material was mounted on microscope slides with Naphrax<sup>®</sup>. In each sample, 600–800 valves were counted using a light microscope (Zeiss Axioplan, oil-immersion Plan-Apochromat objective, aperture 1.4, magnification 1,000×). The identification of diatoms is based on Krammer and Lange-Bertalot (1986, 1988, 1991a, b); Lange-Bertalot and Moser (1994); Krammer (1997a, 1997b) and Scheffler et al. (2005). To examine changes in diatom diversity, the absolute number of species and the diversity index Hill's N2 (effective number of species) were calculated (Hill 1973).

Diatom-inferred TP (Di-TP) values were determined using maximum likelihood (Harris and Stocker 1998). The TP training set data were log 10-transformed. The training set is a

**Table 1** Morphological and limnological characteristics of Lake Dudinghausen

Lake surface area	188,000 m <sup>2</sup>
Lake volume	1,286,874 m <sup>3</sup>
Maximum depth	15.2 m
pH	7.5–8.5
Specific conductivity	350–500 $\mu\text{S cm}^{-1}$
TP	0.02–0.07 mg l <sup>-1</sup>
NO <sub>3</sub> -N	<2.8 mg l <sup>-1</sup>
Secchi depth	1.0–2.0 m
Chlorophyll <i>a</i>	<8.0 $\mu\text{g l}^{-1}$
Phytoplankton biomass	<7.0 mm <sup>3</sup> l <sup>-1</sup>

Limnological data represent annual mean values during 1995–1998 (based on monthly measurements). Chemical and biological water parameters are based on samples from 1 m water depth

combination of a data set from different lakes in Mecklenburg (Adler, S. and Hübener, Th. unpublished, 86 lakes) in combination with the TP data set of the European Diatom Data Base Initiative (EDDI, 343 lakes) (cross validation method: bootstrapping, root mean squared error [RMSE] = 0.30108, root mean squared error of prediction [RMSEP] = 0.33357, squared correlation between inferred and observed values [ $r^2$ ] = 0.7464). Di-TP was calculated with the C2 software. For the EDDI data sets and C2 software see the EDDI homepage “<http://www.craticula.ncl.ac.uk/Eddi/jsp/index.jsp>” and Juggins (2003). The zones of the core were derived from the changes of Di-TP.

### Pigment analyses

To avoid pigment loss or degradation, the sediment samples for pigment analyses were frozen ( $-40^{\circ}\text{C}$ ) in blackened, air-tight and full-filled containers immediately following sediment collection. Due to the varying sediment water content with burial depth, the samples were freeze-dried (lyophilized) under a hard vacuum ( $<0.1$  Pa). Freeze-drying of sediment samples has been shown to improve pigment extraction (e.g., Buffan-Dubau and Carman 2000; Leavitt and Hodgson 2001). Throughout the procedure samples were protected from light, heat and oxygen wherever possible and stored at  $-20^{\circ}\text{C}$ . To prevent pigment transformation or destruction, the samples were extracted immediately upon lyophilisation.

Approximately 40 mg of freeze-dried sediment were suspended with 3–4 ml dimethyl-formamide (p. a., Roth) over night at  $4^{\circ}\text{C}$  (Porra et al. 1989). After addition of saturated sodium chloride solution, the mixture was re-extracted three times with diethyl-ether using a centrifuge (5 min, 6,000 round  $\text{min}^{-1}$ ) to re-extract the pigments. The ether portions were pooled and the solvent was evaporated under a nitrogen stream. The residue was dissolved in 1 ml methanol (HPLC [high performance liquid chromatography] gradient grade, Roth) using the HPLC-autosampler Agilent (Series 1100). Due to the large number of metabolic compounds and derivatives in the sediments, it was necessary to develop a longer HPLC method

for pigment separation modified after Wright et al. (1991). The pigments were isolated and quantified at  $25^{\circ}\text{C}$  by injection of  $50\ \mu\text{l}$  on a  $250 \times 4$  mm C-18 column (Knauer Hypersil,  $5\ \mu\text{m}$ ) with  $5 \times 4$  mm precolumn at a flow of  $0.8\ \text{ml}\ \text{min}^{-1}$  using the following gradient programme: (minutes; % solvent A = 80:20 (v/v) methanol: 0.5 M ammonium acetate; % solvent B = methanol; % solvent C = acetone): (0; 80; 20; 0), (2; 60; 40; 0), (40; 15; 68; 17), (51; 0; 80; 20), (61; 0; 50; 50), (66; 0; 50; 50) (HPLC, Roth). The system was adjusted to the starting conditions within 4 min, the post time for recondition of the column took 5 min. Pigments (chlorophyll *a*, chlorophyll *b*, phaeophytin *a*, phaeophorbide *a*, lutein,  $\beta$ -carotene, zeaxanthin, echinenone and fucoxanthin) were detected by ultraviolet and visible absorption spectroscopy (UV–VIS) with a diode array detector at 440 nm, and at 486 nm for okenone. Spectra were taken from 350 to 800 nm. The standard compounds were obtained usually from Sigma (chlorophyll *a*, chlorophyll *b*, lutein,  $\beta$ -carotene), from Roth (zeaxanthin), from DHI (Danish Hydraulic Institute) Water and Environment (echinenone) and from Prof. Overmann, University of Munich, Institute of Microbiology (okenone). Chlorophyll *a* was converted partially into chlorophyllide *a* by storage in acetone. Their derivatives phaeophytin *a* and phaeophorbide *a* were prepared by acidification (Brotas and Plante-Cuny 1996). The pigment detection limits were at  $5\ \text{ng}\ \text{l}^{-1}$ .

To detect changes in hypolimnetic oxygen levels, three pigment-based indicators were used in this study: (1) the okenone concentration, (2) the ratio of chlorophyll derivatives to total carotenoids (CD/TC\* ratio) and (3) the ratio of chlorophyll *a* to chlorophyll *a* derivatives (Chl *a*/CD).

(1) The carotenoid okenone is specific for only a few species of purple sulphur bacteria (Chromatiaceae; anaerobic phototrophic bacteria), including *Chromatium* spp. (Lami et al. 2000a). This organism occurs at the chemocline of stratified lakes and is present only in anoxic water, rich in  $\text{H}_2\text{S}$  (Züllig 1986). Therefore, the occurrence of okenone provides evidence for permanent or transitory hypolimnetic anoxic conditions (Züllig 1986; Lami et al. 2000a). Furthermore, the okenone concentration was used to indicate the abundance of sulphur bacteria in Lake

Dudinghausen, as okenone is known as a relative stable pigment in lake sediments (Hodgson et al. 1998; Leavitt and Hodgson 2001).

(2) Pigment degradation processes differ between chlorophylls and carotenoids (Yacobi et al. 1991; Leavitt and Hodgson 2001) as chlorophyll degrades more easily under high oxygen levels than carotenoids (Reuss 2005). Carotenoids are often transformed to *cis*-carotenoids in lake sediments and are inherently more stable than intact chlorophylls (Damsté and Koopmans 1997; Reuss 2005) and similarly stable compared to the degradation products of chlorophyll (phaeophytin and phaeophorbide) (Hurley and Armstrong 1990; Yacobi et al. 1991). Thus, decreasing oxygen levels will lead to relatively low CD levels and therefore to decreasing CD/TC\* ratios (Rybak 1988; Ryves et al. 1996; Lami et al. 2000a). In the sediments of Lake Dudinghausen, the only traceable chlorophyll derivatives were phaeophytin *a* and phaeophorbide *a*, whereas all quantitative important carotenoids (lutein,  $\beta$ -carotene, zeaxanthin, echinenone and fucoxanthin) are included in the total carotenoids.

(3) Degradation of chlorophyll include oxidation (allomerisation) and loss of  $Mg^{2+}$  (conversion to phaeophytin) and loss of phytyl chain and various side groups (conversion to phaeophorbide) (Hendry et al. 1987; Scheer 1991). Under anoxic conditions, chlorophyll degradation in sediments is often less rapid (Hurley and Armstrong 1990; Yacobi et al. 1991; Leavitt and Hodgson 2001). Thus, under low oxygen levels more chlorophyll than its derivatives should accumulate in the sediments. Therefore, decreasing oxygen levels should lead to increasing ratios of chlorophyll to its derivatives. We therefore propose that the ratio of chlorophyll *a* to its derivatives phaeophytin *a* and phaeophorbide *a* (Chl *a*/CD) should be a reliable paleo-proxy for oxygen levels. Furthermore, we used this specific ratio (Chl *a*/CD) because phaeophytin *a* and phaeophorbide *a* were the only detectable chlorophyll derivatives in the sediments of Lake Dudinghausen.

#### Chemical sediment analyses

Total nitrogen (TN), total carbon (TC) and organic carbon (org-C; after acidification with 0.1 M

HCl) were analysed from dry weight with a C/N analyser (HERAEUS elementar vario EL) according to Verardo et al. (1990). Inorganic carbon (inorg-C) was calculated as the difference between TC and org-C. The sulphur content was investigated with a C/S-Analyser (“Multi-EA-2000” Analytik Jena) following combustion at 1,300°C and IR (infrared) detection.

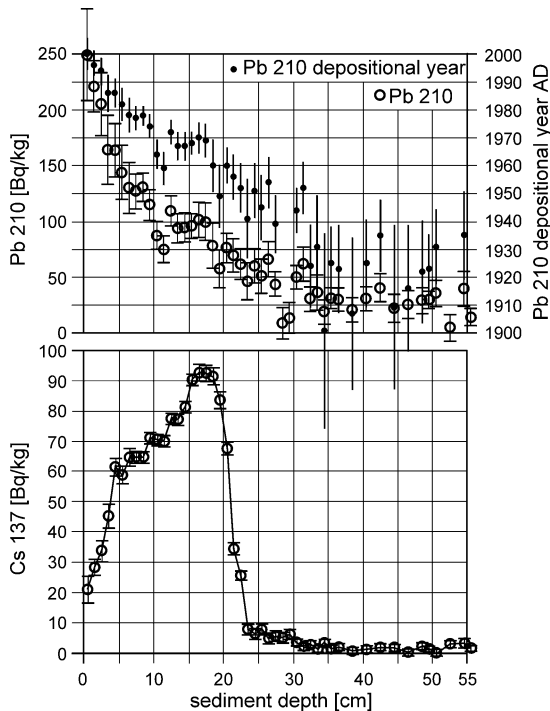
For the analyses of Al, Ca, Fe and Mn, the sediment samples were freeze-dried and homogenized prior to digestion. 500 mg of sample material was completely digested by a cocktail of hydrofluoric, hydrochloric, perchloric and nitric acids (HF/HCl and  $HClO_4/HNO_3$ ) in pressure bombs (35 bar) at 180°C for 3 h. The solution was then evaporated at a heating plate to dry. The residues were dissolved by 5 ml HCl (18 %) and filled up to 50 ml with  $H_2O$ . This solution was used for element analyses. The quantitative analyses of the elements were performed with an Inductive Coupled Plasma-Optical Emission Spectrometer (ICP-OES) Varian Liberty 200 device (Gingele and Leipe 1997). The analytical procedures were validated using certified reference materials (MESS-2, ABSS-1, MBSS-1). Titrisol standards ( $1,000\text{ mg l}^{-1}$ ) from Merck were used for calibration purposes.

## Results

### Chronology

The  $^{210}Pb$  and  $^{137}Cs$  profiles provided a reliable chronology. The  $^{210}Pb$  profile showed a typical exponential decline curve (Fig. 2), suggesting that sediment mixing, either by bioturbation or by physical processes, was not a problem. On the basis of the CRS model, a sedimentation rate was calculated to  $\sim 0.7\text{ cm year}^{-1}$ . The sediment core contains a well resolved  $^{137}Cs$  minor peak (5–7 cm) (Fig. 2) that recorded the fallout from the 1986 Chernobyl accident. A second  $^{137}Cs$  major peak at 17–18 cm recorded the 1963/64 fallout maximum (atmospheric testing of nuclear weapons). At 23 cm  $^{137}Cs$  activity increased steeply and may correlate to the onset of  $^{137}Cs$  fallout ( $\sim 1954$ ). Therefore, the  $^{137}Cs$  chronology is in good agreement with the  $^{210}Pb$  chronology (Fig. 2).





**Fig. 2**  $^{210}\text{Pb}$  and  $^{137}\text{Cs}$  profiles of Lake Dudinghausen. The  $^{210}\text{Pb}$  chronology was calculated using the Constant Rate of Supply (CRS) model. Error bars represent 95% confidence intervals. Dating errors include the statistical error of measurements and error of age calibration

According to the  $^{210}\text{Pb}$  and  $^{137}\text{Cs}$  activities, the whole core (56 cm) represents ~80 years.

### Diatoms

Changes in the Di-TP levels identified five zones. Zone I (52–48 cm, before ~1922) had the lowest Di-TP of the whole core and suggest mesotrophic conditions ( $13.5\text{--}18.7\ \mu\text{g l}^{-1}$ ) (Fig. 3). The diatom assemblage was dominated by the mesotrophic *Cyclotella comensis* Grunow (33–46%) (Fig. 3). Planktonic diatoms made up 49–57%, while periphytic diatoms (e.g., *Fragilaria brevistriata* Grunow and *Amphora inariensis* Krammer) increased from 17 to 30% in this zone (Fig. 3). The number of diatom species was the highest in the entire sediment core (72 species at 50 cm, Fig. 3). The diversity (Hill's N2) increased from 4.2 (52 cm) to 7.7 (48 cm) (Fig. 3).

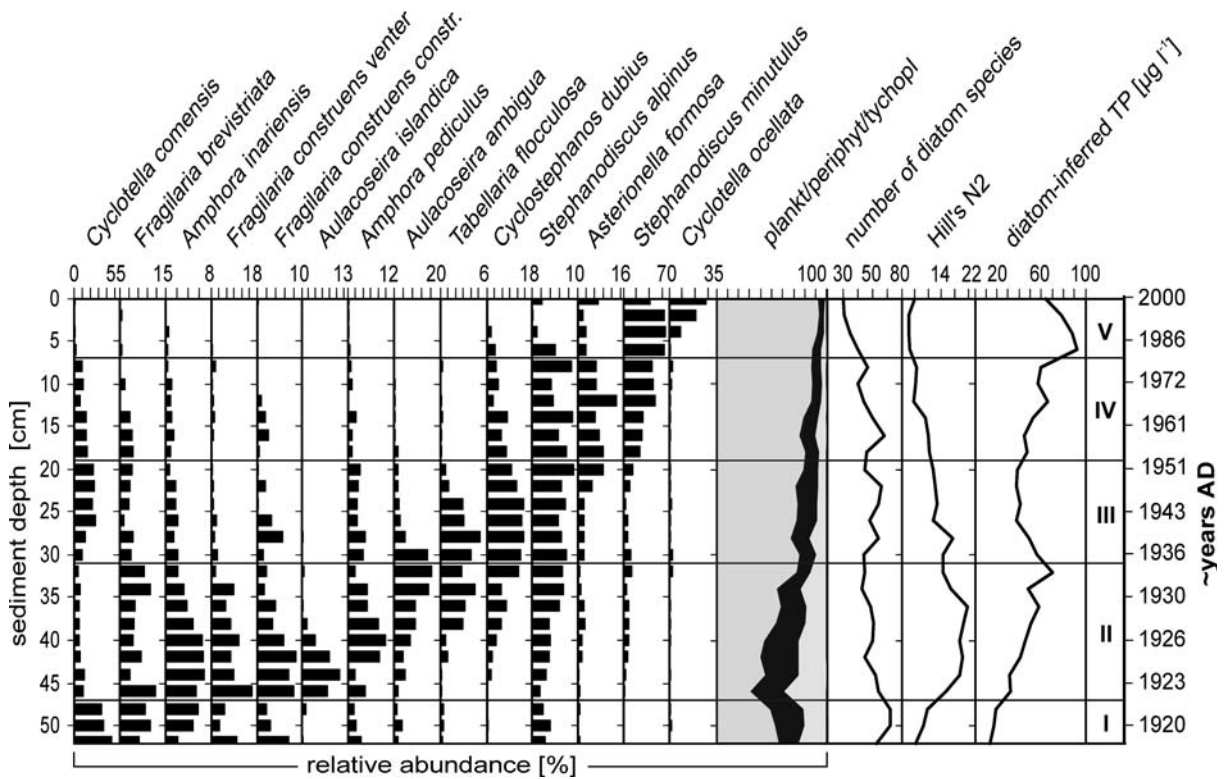
In Zone II (46–32 cm, ~1923–1935), the Di-TP increased continuously up to moderate eutrophic conditions (from 32 to  $70\ \mu\text{g l}^{-1}$ ). The relative

abundance of *Cyclotella comensis* decreased to 5% and was replaced by eutrophic diatoms such as *Stephanodiscus minutulus* (first appearance at 46 cm), *Aulacoseira islandica* (O. Müller) Simonsen (>10% at 44 cm), *Aulacoseira ambigua* (Grunow) Simonsen (>16%), *Cyclostephanos dubius* (Fricke) Round, *Tabellaria flocculosa* (Roth) Kützing and *Stephanodiscus alpinus* Hustedt (Fig. 3). Additionally, benthic diatoms such as *Amphora inariensis*, *A. pediculus* (Kützing) Grunow, *Fragilaria construens* f. *venter* (Ehrenberg) Hustedt and *F. construens* f. *construens* (Ehrenberg) Hustedt increased (Fig. 3). Planktonic taxa decreased to their core minimum (31% at 46 cm). In the remaining core planktonic taxa continuously increased up to 93% at 0–1 cm. The number of diatom species decreased from 64 to 53. However, the diatom diversity was particularly high, indicated by the highest Hill's N2 (12.4–19.9) of the entire sediment core.

Zone III (30–20 cm, ~1936–1951) is characterised by decreasing Di-TP levels (to low eutrophic conditions of  $37\text{--}38\ \mu\text{g l}^{-1}$ ). *Cyclotella comensis* increased again to 26%, while eutrophic diatoms (e.g., *Stephanodiscus minutulus*, *Asterionella formosa* Hassall, *Aulacoseira ambigua*, *Tabellaria flocculosa* and *Cyclostephanos dubius*) decreased. The number of diatom species varied around 55–66 (from 28 to 20 cm). Simultaneously, the diversity continuously decreased from 15.3 to 9.6 in this zone.

The Di-TP levels increased again to moderate eutrophic conditions ( $>60\ \mu\text{g l}^{-1}$ ) in Zone IV (18–8 cm, ~1952–1980). Consequently, *Cyclotella comensis* decreased from 17 to 8%. At the same time eutrophic diatoms increased, e.g., *Stephanodiscus minutulus* (25–49%) and *Asterionella formosa* (1–6%). *Cyclostephanos dubius* decreased from 8 to 4%. The number of species and Hill's N2 continued to decrease in this zone and in Zone V to 40 and 3.9, respectively, at 0–1 cm.

Di-TP decreased again in Zone V (6–0 cm, ~1981–2000), but remained high ( $64\ \mu\text{g l}^{-1}$ ). *Cyclotella comensis* decreased to 0.6%. The eutrophic conditions continued as indicated by only a slight decrease of eutrophic diatoms as *Asterionella formosa* and *Stephanodiscus alpinus*. *Cyclostephanos dubius* was not found in the upper sediment. *Cyclotella ocellata*, a meso- to



**Fig. 3** Main diatom taxa, diatom life forms, number of diatom species, Hill's N2 index and diatom inferred TP (Di-TP) of Lake Dudinghausen. The age scale is based on <sup>210</sup>Pb (see Fig. 2). Zonation was set according to changes

in Di-TP. Abbreviations of diatom life forms: plankt. = plankton; periphyt. = periphyton; tychopt. = tychoplankton. Note: All x-axes start with 0 except number of diatom species (starts with 30) and Hill's N2 (starts with 3.5)

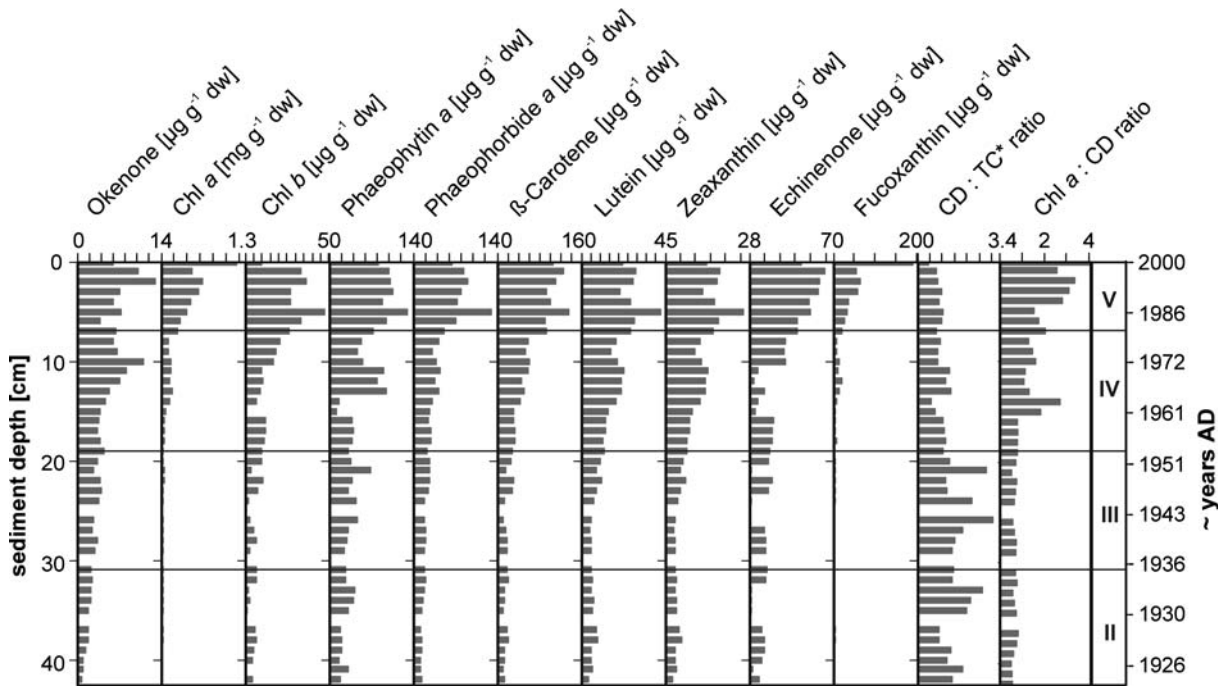
eutraphentic diatom, appeared in the sediment for the first time (Fig. 3). Together with *Stephanodiscus minutulus* (41%), *C. ocellata* (28%) dominated the assemblage at 0–1 cm. This “new” diatom flora of the upper sediment layers has not been recorded in older sediments of Lake Dudinghausen, including a long core representing the last ~4,800 years (Dreßler et al. 2006).

**Pigments**

Pigment content of the sediment was relatively low in the diatom Zones I–III (42–20 cm; Fig. 4). In the surface 20 cm of the core (diatom Zones IV and V), four different patterns were observed: (1) The Chl *a*, echinenone and fucoxanthin content of the sediment continuously increased from 20 to 0 cm; (2) Chl *b* content increased to a core maximum at 5 cm, remained high from 5 to 1 cm and, finally decreased in the surface sediment

(0 cm); (3) In contrast to echinenone and Chl *b*, the carotenoids lutein, zeaxanthin, fucoxanthin and β-carotene, as well as the decomposition products of Chl *a* (phaeophytin *a* and phaeophorbide *a*), had additional, minor peaks at 11–13 cm; (4). Finally, the sulphur bacteria pigment okenone increased from 20 to 10 cm. However, in contrast to the fossil algal pigments (patterns 1–3), the okenone concentrations continuously decreased from 10 to 6 cm. Okenone increased again from 5 to 2 cm and decreased in the upper 2 cm of the sediment core.

The ratio of chlorophyll derivatives to total carotenoids (CD/TC\*) varied between 1 and 3.4 from 42 to 21 cm. In the upper 20 cm, the CD/TC\* ratio was lower than 1.0 (Fig. 4). The ratio of Chl *a* to its derivatives phaeophytin *a* and phaeophorbide *a* (Chl *a*/CD) was low from 42 to 16 cm (<1). At 15–14 cm sediment depth, the Chl *a*/CD ratio increased sharply, and varied



**Fig. 4** Fossil pigments of Lake Dudinghausen. For age scale and zonation see Figs. 2 and 3. CD = chlorophyll derivatives; TC\* = total carotenoids. For further details see the text

with relative high values between 1 and 4 at 13–0 cm.

#### Chemical sediment parameters

The nutrient and metal concentrations followed four different patterns throughout the core (Fig. 5): (1) total carbon content decreased from 55 to 35 cm (diatom Zone II) and slowly increased again towards the surface of the core (0 cm); (2) organic carbon, Al, Fe content as well as Fe/Mn and Fe/Ca ratios increased from 55 to 40 cm (also diatom Zone II) and continuously decreased again towards the surface of the core; (3) inorganic carbon, C/N ratio, Mn and Ca content followed the opposite pattern to (2) with a minimum concentration at 40 cm; (4) S concentration was highest at 35 cm and 12 cm (Fig. 5).

## Discussion

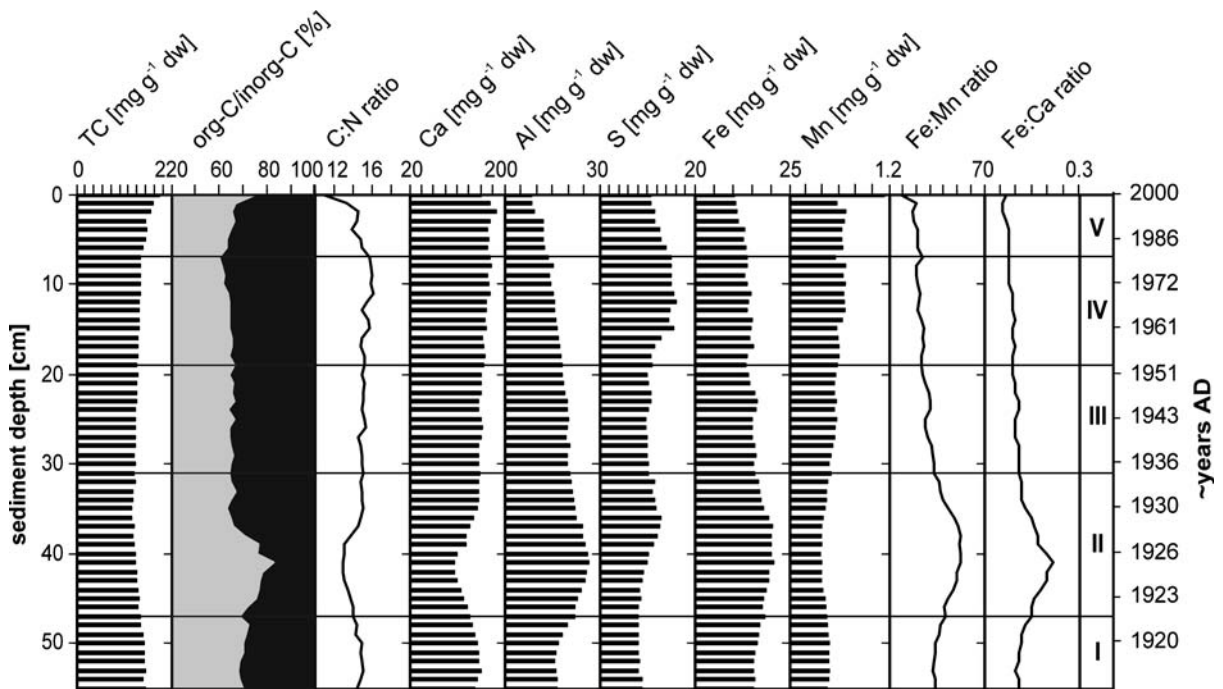
### Trophic development

Before ~1922 (Zone I): Human influence on the trophic of the lake was not detectable. Di-TP

indicates stable mesotrophic conditions (Figs. 3 and 6). Similarly, the high abundance of periphytic diatoms suggests that deeper water regions of the lake were available for photosynthetic growth and thus points to a high light penetration. Despite the high number of species (in relation to younger sediment layers) the Hill's N2 was low, which suggests that only a few diatom species had been important for the relatively undisturbed diatom flora.

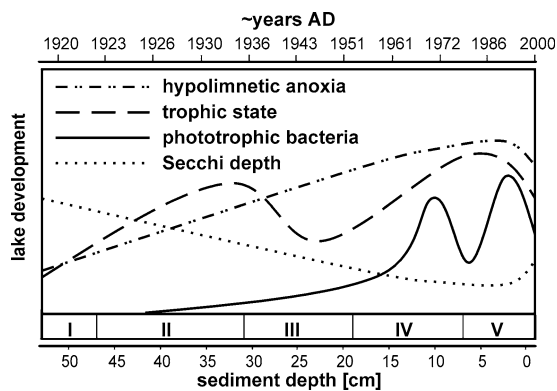
Between ~1923–1935 (Zone II): At this time the Di-TP increased continuously to eutrophic conditions suggesting a gradual increase of cultural eutrophication. The number of diatom species decreased and the Hill's N2 index increased, which suggests a relatively unstable diatom flora probably due to an increased nutrient input (e.g., marked change from dominance of *Cyclotella comensis* to *Aulacoseira islandica* and *A. ambigua*). In contrast, the reason for the increased abundance of small *Fragilaria* species, such as *F. brevistriata*, *F. construens* f. *construens* and *F. construens* f. *venter* (see Wolin and Duthie 1999; Lotter et al. 2000), is unclear; it could bear a reference to an increase in trophic status or to





**Fig. 5** Chemical sediment parameters and metal ratios of Lake Dudinghausen. TC = total carbon; org-C = organic carbon; inorg-C = inorganic carbon. For age scale and

zonation see Figs. 2 and 3. Note: All x-axes start with 0 except C/N ratio (starts with 10)



**Fig. 6** Development of Lake Dudinghausen based on sedimentary diatoms, fossil algal pigments and okenone, geochemical sediment parameters and metals during the last approx. 80 years. For age scale and zonation see Figs. 2 and 3. For further details see the text

changes in climate conditions (Lotter et al. 2000). Furthermore, the number of planktonic diatoms increased continuously, which is often used as an indicator of water level fluctuations (Wolin and Duthie 1999), however the increase in planktonic diatoms and the decrease of benthic diatoms may suggest decreasing light penetration concurrent

with decreasing macrophyte abundances. Simultaneously with rising Di-TP, an intensified storage of sulphur occurred in the sediment, which has also been observed in other investigations of lake eutrophication (Alvisi and Dinelli 2002).

Between ~1936–1951 (Zone III): At this time a partial recovery of the lake’s trophic state is indicated by the decreasing Di-TP values (Fig. 3). The eutraphentic *Tabellaria flocculosa* was abundant, which was also observed during phases of decreasing nutrient levels in other investigations of eutrophic lakes (Hall et al. 1999a). Accordingly, the Di-TP decreased, however a complete lake-regeneration back to mesotrophic conditions did not take place. The lake was still slightly eutrophic. Similarly, decreasing Al and Fe values suggest reduced exogenous mineral inputs due to increased soil stabilisation and decreased erosion, and therefore also suggest decreasing nutrient load as well as a reduction of agricultural activity in the lake’s catchment. A possible reason for this decreased nutrient enrichment could be the influence of the Second World War on agriculture in this region.

Between ~1952–1980 (Zone IV): A much higher nutrient load than in Zone III and an increased eutrophic state is indicated by continuously increasing Di-TP values. The high Di-TP levels were mainly due to the increasing dominance of the eutrathentic *Stephanodiscus minutulus*, which previously only occurred in low numbers. The number of diatom species and also the Hill's N2 index decreased, and a stable typically eutrathentic diatom flora was established. The clear dominance of planktonic diatoms indicate a further reduction of light penetration.

Complementary to diatoms, the algal pigments suggest increasing bioproduction in the lake as concentrations of most fossil algal pigments increased during Zone IV (Fig. 4) and reached values typical of eutrophic lakes (Cuddington and Leavitt 1999; Hall et al. 1999b; Lami et al. 2000a, b). For example,  $\beta$ -carotene increased in this zone (Fig. 4), suggesting increased total algal abundance (Cuddington and Leavitt 1999), as  $\beta$ -carotene is a chemically stable, ubiquitous carotenoid (Leavitt and Hodgson 2001; Reuss 2005). Similarly increased concentration of lutein and Chl *b* (typical for chlorophytes, euglenophytes and trachaeophytes) indicate increasing abundance of green algae (Leavitt and Hodgson 2001) as macrophytes and euglenophytes are not very common in Lake Dudinghausen. Elevated concentrations of Chl *b* suggest that this pigment was not derived from terrestrial sources because Chl *b* from land plants is degraded prior to deposition (Lami et al. 2000a). Zeaxanthin and echinenone indicate increasing dominance of planktonic cyanobacteria typical for eutrophic lakes (Leavitt and Hodgson 2001).

The relatively high C/N ratio suggests that more organic material in the sediment is of terrestrial origin (Meyers et al. 1993). Altogether, the increased nutrient levels in Lake Dudinghausen were probably due to more intensive agricultural cultivation and the drainage of large areas at this time. Similar trends were observed in other investigations (e.g., Alvisi and Dinelli 2002).

Between ~1981–2000 (Zone V): Reduced bioproduction was inferred in this zone as the Di-TP decreased again, but remained in the eutrophic range. As planktonic diatom species remained

dominant, light penetration would still be relatively low. For the first time, the plankton is dominated by the eutrathentic *Stephanodiscus minutulus* and, with decreasing Di-TP, by the meso- to slightly eutrathentic *Cyclotella ocellata*. Furthermore, typical diatoms for older sediments (Dreßler et al. 2006) have become absent or unimportant (e.g., *Cyclotella comensis*, *Fragilaria brevistriata*, *Amphora inariensis*, *A. pediculus*, *Aulacoseira ambigua*, *Fragilaria construens* f. *venter* and *F. construens* f. *construens*). This completely new diatom composition was unique to these surface sediments.

The algal pigments, mainly Chl *a* and  $\beta$ -carotene (all algae), Chl *b* and lutein (green algae), echinenone and zeaxanthin (planktonic cyanobacteria) and fucoxanthin (dinophyta, bacillariophyta and chrysophyta) are present in high concentrations in Zone V and thus suggest a relatively high bioproduction (Engstrom et al. 1985; Waters et al. 2005). However, the drastic decrease of Al suggests decreasing mineral input and therefore decreasing agriculture. This phase of slightly improving trophic state of the lake approximately corresponds to the political changes in 1989, after which agricultural methods changed again from collective agricultural systems (United Agricultural Cooperatives and State Farms) to individual farmer systems (Van Rompaey et al. 2003).

Redox conditions at the sediment-water interface and hypolimnetic anoxia

Changes in the Fe/Mn and Fe/Ca ratios in the sediments are linked to changing redox conditions at the sediment surface (Wersin et al. 1991; Garbe-Schönberg et al. 1998; Itkonen et al. 1999; Loizeauj et al. 2001; Koinig et al. 2003). Generally, increased bioproduction and therefore increased anoxia in deeper waters will lead to a stronger solution of Mn and Ca compared to Fe (the reduced form of Fe is less stable in the water column than those of Mn and Ca) from the sediment, and thus to lower Mn and Ca concentrations in the sediment as well as high Fe/Mn and Fe/Ca ratios. Accordingly, Fe/Mn and Fe/Ca ratios increased during the first phase of eutrophication (Zone II) in Lake Dudinghausen

(Figs. 5 and 6). Thus, Fe was still available as a binding partner for P under oxic conditions. Similar limnetic changes (oxic to anoxic hypolimnion) through eutrophication were observed in other lakes (e.g., Olsson et al. 1997).

Surprisingly, the Fe/Mn ratio did not increase during the second phase of eutrophication (Zone IV; Fig. 5). Possibly, the advanced trophic state led to a more pronounced oxygen depletion above the sediment (temporally and spatially). Thus, both Mn and Fe were equally released from the sediment into the water and therefore the Fe/Mn and Fe/Ca ratios in the sediments did not change.

Increasingly anoxic conditions on the sediment water interface were also supported by the CD/TC\* ratio. Anoxia is related to low CD/TC\* ratios in the sediments (Rybak 1988; Ryves et al. 1996; Lami et al. 2000a). Therefore, anoxia must have intensified after ~1950 (Zone IV) because the CD/TC\* ratio remained low from 20 cm to the surface of the core, while the ratio fluctuated in older sediments, suggesting at least partial oxic conditions (Fig. 4).

The Chl *a*/CD ratio showed an opposite trend to the CD/TC\* ratio, also indicating decreasing oxygen levels, especially after ~1960 (Zone IV). This confirms our assumption that the Chl *a*/CD ratio is also a good indicator of anoxia, as chlorophyll degrades less rapidly under anoxic conditions in lake sediments (Hurley and Armstrong 1990; Yacobi et al. 1991; Leavitt and Hodgson 2001), resulting in better accumulation of chlorophylls than its derivatives under low oxygen levels. This assumption is also supported by the okenone concentration (see below), which follows the trend of the Chl *a*/CD ratio with a slight delay. Thus, it can be said that the Chl *a*/CD ratio in lake sediments can act as an additional, reliable hypolimnetic oxygen proxy in paleolimnology.

#### Occurrence of phototrophic sulphur bacteria

Okenone indicates the presence of phototrophic sulphur bacteria (e.g., Ryves et al. 1996; Lami et al. 2000a, b). A distinct increase of okenone was observed in the core from 14 cm to 10 cm (Zone IV; Figs. 4 and 6). For such mass development of phototrophic sulphur bacteria, four conditions are essential: water stratification, high

trophic state to favour anoxia (release of sulfide), sulfide as substrate (redox potential less than 190 mV), and light energy in greater water depths (Vila and Abella 2001).

Okenone decreased from 10 cm to 6 cm (Fig. 4), despite a continuously increasing trophic state (Figs. 3 and 6). The other indicators suggest a further eutrophication at approx. 10 cm sediment depth (see above), resulting in an increased bioproduction. Therefore, Secchi depths probably decreased and lead to a decrease of phototrophic sulphur bacteria.

From 6 cm to the surface (0 cm), the Di-TP values decreased significantly again and it came to another increase of okenone (Fig. 4). Possibly, the slightly decreased trophic state led to an improvement of Secchi depths and the resulting light conditions favoured another mass occurrence of phototrophic sulphur bacteria. Similarly, other investigations have shown massive occurrences of *Chromatium* spp. in late summer and autumn during the years 1996–2000 in Lake Dudinghausen (Selig et al. 2004). In this recent investigation, phototrophic sulphur bacteria were only observed in the water body above 10 m. Similarly, measurements of the light saturation point ( $=E_k$ ) of the photosynthesis curve versus the irradiance curve in a Swiss lake confirm that at 10 m water depth, the light availability is sufficient for phototrophic sulphur bacteria (Schanz et al. 1998). Phototrophic sulphur bacteria may also stabilise the eutrophic status of a lake. The bacteria accumulate released P from the sediment in their biomass and may thus have acted as a “nutrient filter” in the hypolimnion and inhibited the nutrient release in the epilimnion of the lake. With a further decrease of Di-TP in the surface 3 cm of the core, okenone decreased slightly again. Therefore, okenone also suggest the beginning improvement of the lake’s trophic state in recent years.

#### Conclusions

The various paleoindicators we used in Lake Dudinghausen suggest two different phases of eutrophication coupled with hypolimnetic anoxia during the last ~80 years: a first phase from about

1923–1932 and a second from 1952 to 1982 (Fig. 6). Both phases of eutrophication are probably of anthropogenic origin, because the trophic changes are too abrupt for natural eutrophication and the natural trophic state of Lake Dudinghausen was most likely mesotrophic. Overall, the nutrient levels of the lake have decreased during the last few years, but they are still higher than ~80 years ago. Therefore, a restoration programme could be successful.

Interestingly, a drastic change in the diatom flora was evident for the upper sediment layers, with a diatom flora not previously recorded over the last ~80 years (this study) nor over the last ~4,800 years of Lake Dudinghausen's history (Dreßler et al. 2006). Therefore, a completely new limnological situation has developed, which is not comparable with former lake conditions. Thus, a restoration programme may lead to natural nutrient levels, but will not necessarily lead to overall natural (reference) biological conditions according to the diatom assemblages. Thus, a restoration programme may lead to natural nutrient levels. However, the limnological question remains, why the diatom taxa have changed.

In the first phase of eutrophication of Lake Dudinghausen, the Fe/Mn and Fe/Ca ratios clearly increased and thus suggest seasonal anoxia near the sediment. Surprisingly, however, the Fe/Mn and Fe/Ca ratios decreased while anoxia clearly increased both temporally and spatially during the second phase of eutrophication (as suggested by diatoms, algal pigments, okenone, CD/TC\* and Chl *a*/CD ratios). Possibly, the increased anoxia led to an equally strong reduction of all three metals (Fe, Mn and Ca) from the sediments.

About 80 years ago, and during the first phase of cultural eutrophication, there was no mass development of sulphur bacteria in Lake Dudinghausen as indicated by relatively low okenone levels. However, during the beginning of the second eutrophication phase and during the decreasing nutrient levels in recent years, a mass development of phototrophic sulphur bacteria occurred, suggesting anoxic hypolimnetic conditions. Interestingly, the abundance of sulphur bacteria decreased during the highest levels of eutrophication. This decrease can be attributed to

an increase in nutrient load, which resulted in reduced light penetration and therefore unfavourable conditions for sulphur bacteria. Therefore, the mass developments of phototrophic sulphur bacteria in Lake Dudinghausen do not reflect natural conditions. Instead, the abundant sulphur bacteria represent an intermediate stage of nutrient levels during the development of Lake Dudinghausen, as they require both anoxic conditions in the hypolimnion and sufficient light levels. Therefore, lake management measures to further reduce the nutrient levels in Lake Dudinghausen will lead to decreasing sulphur bacteria abundances.

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