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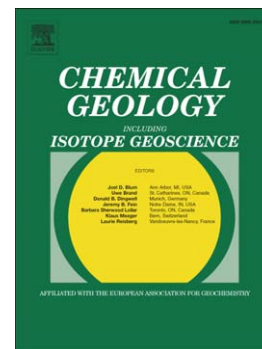
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Compound-specific carbon and nitrogen isotopic compositions of chlorophyll *a* and its derivatives reveal the eutrophication history of Lake Zurich (Switzerland)

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ABSTRACT

To reconstruct the impact of eutrophication on phototrophic communities and the biogeochemical cycling of carbon and nitrogen in the surface water, we investigated the distributions and carbon and nitrogen isotopic composition ($\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values) of chlorins in the sediments of Lake Zurich. The chlorin distributions were dominated by chlorophyll *a* (Chl *a*) and its derivatives, which reflect rapid degradation to the pheopigments in the water column and sediments of the lake. The $\delta^{13}\text{C}$ values of these sedimentary chlorins followed the historical trends of eutrophication and reoligotrophication, except in the surface sediments, which were characterised by higher relative contributions of aged, redeposited organic matter (OM). The $\delta^{13}\text{C}$ values of the sedimentary chlorins together with bulk sediment $\delta^{13}\text{C}$ values and C/N ratios indicate that the phototrophic communities in the lake used a ^{13}C -depleted carbon source, which is mainly of aquatic origin. The $\delta^{15}\text{N}$ values of chlorins reflect the predominance of nitrate assimilating phototrophs, especially the non- N_2 -fixing cyanobacterium *Planktothrix rubescens* prevalent during sediment deposition. Shifts in $\delta^{15}\text{N}$ values of Chl *a* followed mostly the trends in eutrophication and reoligotrophication, but were also affected by community assemblage shifts to diatoms and/or other cyanobacteria at the end of the 19th century and during the eutrophication maximum in the 1970s. The lower $\delta^{15}\text{N}_{\text{Chl-a}}$ values in the surface sediments coincide with increasing nitrogen to phosphorus ratios and reduced water column mixing that characterise the recent reoligotrophication period and may explain the predominance of *P. rubescens* in Lake Zurich. In contrast, the higher contributions of laterally transported OM explains the large offset of $\delta^{15}\text{N}$ values of the pheopigments relative to Chl *a*, which is supported by the high radiocarbon age of the surface sediments.

Keywords: Pigment; chlorophyll; carbon isotope; nitrogen isotope; phytoplankton; Lake Zurich

1. Introduction

Chlorophylls are widespread in aquatic and terrestrial environments and are the main pigments in phytoplanktonic algae, cyanobacteria, aquatic macrophytes and vascular plants (e.g. Keely, 2006; Scheer, 2006). These light-harvesting pigments are vital for photosynthesis and represent the most abundant and most significant pigments on Earth (e.g. Keely, 2006; Scheer, 2006). The primary chlorophylls are subject to a large array of structural transformation and decomposition processes in the water column and the underlying sediments (Bianchi et al., 1993; Furlong and Carpenter, 1988; Louda et al., 1998; Louda et al., 2011). However, despite these pre- and post-depositional structural alterations, chlorophylls and their derivatives in the sedimentary record can be used to reconstruct all groups of phototrophic communities in the past water columns (Keely, 2006).

Pheopigments are primary degradation products of chlorophylls and comprise most notably pheophytins, pheophorbides and pyropheophytins, which are formed by demetallation of the central magnesium ion, by ester hydrolysis and by demethoxycarbonylation, respectively (e.g. Chen et al., 2003; Keely, 2006). A specific chlorophyll *a* derivative is $13^2,17^3$ -cyclopheophorbide-*a*-enol (CPhe *a*), which may be formed by herbivory (Goericke et al., 2000) or within anoxic sediments (Louda et al., 2000). Other derivatives of grazing are steryl and carotenol chlorin esters (SCEs and CCEs), formed by esterification of chloro- and pheopigments with

steroids and carotenoids, respectively (e.g. Chen et al., 2003; Furlong and Carpenter, 1988; King and Repeta, 1991).

Despite these transformation processes, the macrocycle of most tetrapyrroles can be easily preserved (e.g. Higgins et al., 2011; Ohkouchi and Takano, 2014; Sachs et al., 1999). The $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ signatures are anticipated to be not altered significantly during diagenesis, therefore providing a tool to reconstruct the dynamics of phytoplankton communities and biogeochemical processes in surface water environments (Macko and Estep, 1984; 2006; Ohkouchi et al., 2005; Ohkouchi and Takano, 2014; e.g. Sachs et al., 1999; Tyler et al., 2010).

For instance, nitrogen isotopes provide valuable information on nutrient cycling (e.g. Higgins et al., 2011; Ohkouchi and Takano, 2014; Sachs et al., 1999), which controls algal productivity. However, the $\delta^{15}\text{N}$ values of biomass and bulk sediments are prone to significant, unpredictable diagenetic alterations (e.g. Freudenthal et al., 2001; Lehmann et al., 2002; Sigman et al., 1999). In contrast, nitrogen within chloro- and pheopigments remains preserved (e.g. Higgins et al., 2011; Sachs et al., 1999; Tyler et al., 2010). Therefore, compound-specific isotope analysis of pigments can provide specific information of the biogeochemical cycling of carbon and nitrogen in the photic zone of aquatic/ marine waters (e.g. Hayes et al., 1990; Higgins et al., 2011; Ohkouchi et al., 2005; Tyler et al., 2010).

Recent developments have led to significant improvements of analytical techniques to purify chloro- and pheopigments from sediment extracts and to analyse their carbon and nitrogen isotopic composition (Higgins et al., 2009; Ogawa et al., 2010; Polissar et al., 2009; Sachs and Repeta, 2000). Therefore, these techniques facilitate investigations of historical changes in carbon and nitrogen cycling mediated by phototrophs in the surface water of lakes and oceans as a response to changing environmental and climatic conditions (summarised by Ohkouchi and Takano, 2014).

In order to learn more about these processes, we studied Lake Zurich, located within a highly populated region in Switzerland, including the City of Zurich (> 400,000 inhabitants), and providing drinking water for about 1.5 million people. The lake has been thoroughly investigated during the last century until now, including a unique monitoring program, which started in 1936 and comprises mostly monthly data resolution for various parameters including temperature and oxygen at 19 different depths (typically 0.3, 1, 2.5, 5, 7.5, 10, 12.5, 15, 20, 30, 40, 60, 80, 90, 100, 110, 120, 130 and 135 m). Details on the monitoring dataset were reported in Zimmermann et al. (1991), Livingstone (2003) and Jankowski et al. (2006).

The aim of this study was the reconstruction of the impact of eutrophication and climate on the biogeochemical cycling of carbon and nitrogen mediated by phytoplankton communities within the lake's surface water for more than the last century.

2. Materials and methods

2.1. Study site and sample collection

The pre-alpine, mesotrophic Lake Zurich (Lower Lake; Fig. 1) has a surface area of 67.3 km², a volume of 3.3 km³, a maximum depth of 137 meters and lies at 406 meters above sea level (Wieland et al., 2001). The lake basin is orientated from the southeast to the northwest and the lake is of glacial origin (Kelts, 1978). A moraine sill (maximum water depth of 3 m) divides the lake into two lake basins (Upper and Lower Lake Zurich; Fig. 1) and the Upper Lake acts as a settling basin of main allochthonous riverine supply from the Linth River (e.g. Livingstone, 2003; Wieland et al., 2001). The water residence time is about 1.5 yr (Wieland et al., 2001). The lake is

monomictic or dimictic depending on the prevailing winter conditions, but it recently tends to become oligomictic due to climate change (Friedrich et al., 2014; Livingstone, 2003; North et al., 2014).

The lake was originally oligotrophic (Züllig, 1982), but underwent strong eutrophication up to the 1980s (Bossard et al., 2001). Both monitoring data and manganese to iron ratio indicated generally low concentration of dissolved oxygen before 1955 as a result of eutrophication (Naehler et al., 2013). Although wastewater treatment plants have been constructed since 1955, phosphate concentrations did not decrease until the 1970s when improved phosphorus removal and a phosphate ban in detergents led to a progressive decrease of phosphate concentrations in the lake water, resulting in a change from an eutrophic to mesotrophic state (Bossard et al., 2001; Jankowski et al., 2006). Furthermore, the recent oligotrophication of the lake together with increasing air and water temperatures related to climate change has led to reduced water column mixing and reduced bottom water oxygen renewal (Livingstone, 2003; North et al., 2014; Posch et al., 2012).

The sediment samples studied from the lower (main) lake originated from two cores obtained with a gravity corer at the maximum depth of 137 meters (Fig. 1) in November 2009 (samples between 0 and 10 cm depth; core ZH-09-05; 110 cm long; 47°17.004'N, 8°35.640'E, WGS84) and in November 2010 (samples between 20 and 40 cm depth; core ZH-10-18; 105 cm long; 47°17.153'N, 8° 35.506'E, WGS84). Samples for bulk parameters (total organic and inorganic carbon, total nitrogen, stable isotopic compositions of total organic carbon and total nitrogen), chlorin index and total chlorin concentrations were obtained from the laminated parts of core ZH-09-05. The age models for the studied cores were established based on varve counting and the average sedimentation rates are ca. 0.28 cm yr⁻¹, which is in agreement with estimates on an equivalent core described in Naehler et al. (2013).

2.2. Phytoplankton communities

The phytoplankton in Lake Zurich is typically characterised by diatoms (especially *Stephanodiscus hantzschii*) and flagellates (*Rhodomonas*, *Cryptomonas*) when the lake becomes stratified in spring (Bleiker and Schanz, 1997). After the clear-water phase (corresponding to low algal densities due to zooplankton grazing), colony forming diatoms (mainly *Asterionella formosa*, *Aulacoseira granulata* and *Fragillaria crotonesis*) as well as green algae, including flagellates in certain years, become dominant (Bleiker and Schanz, 1997). Overall, the dominating algae in the lake include diatoms and cryptophyta, whereas chlorophyta account for less than 10% of phytoplankton biomass (Bossard et al., 2001).

However, the non-N₂-fixing cyanobacterium *Planktothrix rubescens* ("burgundy blood algae") has become the dominant species in the lake during the last four decades (Posch et al., 2012). In late summer, it occurs in masses in water depths between 10 and 12 m and is typically abundant throughout the epilimnion in fall (Bossard et al., 2001). *P. rubescens* accounts for more than 50% of the total phytoplankton biomass from September to March and in recent years it persists throughout the year (Bossard et al., 2001; Posch et al., 2012). Other cyanobacteria in the lake comprise *Microcystis*, *Aphanizomenon*, *Aphanothece* and *Aphanocapsa* (Bossard et al., 2001). In some years, also blooms of *Aphanizomenon flos-aquae* have been observed (F. Schanz, personal communication, 2015).

The first large phytoplankton blooms in Lake Zurich were reported in 1896 and 1898, which were dominated by the diatom *Tabellaria fenestrata* and *P. rubescens*, respectively (Hasler, 1947; Minder, 1938). These blooms coincide with the onset of a laminated sedimentary record and that has lasted until the present day, associated

with pronounced, at least seasonal bottom water anoxia (e.g. Naeher et al., 2013; Züllig, 1982; 1989). Prior to the first bloom of *Tabellaria fenestrata*, *Asterionella formosa* and *Fragillaria crotonensis* were predominant in the sediments of 1985 (Züllig, 1982). In contrast, first cyanobacterial blooms in 1897 consisted mainly of *Microcystis* and *Anabaena* species, whereas *P. rubescens* first appeared in 1898 (Hasler, 1947; Minder, 1938; Schröter, 1897). Since then *P. rubescens* has been regularly observed until 1964, but was low or absent during the lake's maximum eutrophication and again common since the late 1970s (Posch et al., 2012; Züllig, 1989). The recent reoligotrophication due to the associated decrease in phosphate concentrations together with higher water temperatures and the associated reduced water column mixing has facilitated the predominance of *P. rubescens* in Lake Zurich (Posch et al., 2012).

2.3. Bulk parameter analyses

Bulk sediment parameters (total organic and inorganic carbon, total nitrogen, bulk sediment $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values) and chlorin indices were analysed under the same conditions using the same instrument as reported in Naeher et al. (2012).

The chlorin index and total chlorin concentrations were analysed as reported in Schubert et al. (2005). This index is a measure of the degree of degradation of labile organic matter (OM) and defined as the ratio between the fluorescence intensity of a sediment extracted with acetone and treated with hydrochloric acid (1M HCl) and the original sediment extract, using 428 nm and 671 nm as excitation and emission wavelengths, respectively. Typical values of chlorin index range between 0.2 for fresh material and 1.0 for degraded, inert material (Schubert et al., 2005).

2.4. Extraction, isolation and compound-specific carbon and nitrogen isotopic analyses of sedimentary chlorins

The chlorins in the sediments from Lake Zurich were analysed according to the method described in Tyler et al. (2010) with some additional modifications as reported in Naeher et al. (2016). In short, freeze dried and ground sediment (2-4 g) was extracted using acetone (3x with twice the sample volume) by ultrasonication for 15 min in an ice bath, followed by centrifugation at 777×G for 5 min. After liquid-liquid separation in a *n*-hexane-MilliQ bilayer (ratio 1:3), the lipid extract was dried under reduced pressure and samples were stored within an argon atmosphere at -20°C. All steps were carried out under careful exclusion of light irradiation where possible. For analysis, samples were dissolved in *N,N*-dimethylformamide and centrifuged at 12,225×G for 90 s to remove particles.

The pigments were analysed by reversed-phase high performance liquid chromatography (HPLC), using an Agilent Infinity 1260 series HPLC equipped with a photodiode array detector (DAD) and fraction collector. Chlorin separation was achieved using an Agilent Eclipse XDB-C18 column (250 mm × 4.6 mm; 5 µm) and an Agilent Eclipse XDB-C18 guard column (12.5 mm × 4.6 mm; 5 µm). The pigments were eluted isocratically with 75% A and 25% B for 5 min and then with a linear gradient to 50% B for 50 min at 1.0 ml min⁻¹, where A = acetonitrile/pyridine (100:0.5; v:v) and B = ethyl acetate/pyridine (100:0.5; v:v). The oven temperature was kept constant at 30°C.

Purification of the isolated chlorins (second fraction collection) was achieved using an Agilent Eclipse PAH column (250 mm × 4.6 mm; 5 µm) with an Agilent Eclipse PAH guard column (12.5 mm × 4.6 mm; 5 µm). Pigments were eluted isocratically using 20% B for 5 min, followed by a linear gradient to 60% B for 30 min and then to 100%

B for 13 min. The flow rate was constant at 1.0 ml min⁻¹. The oven temperature was kept at 15°C for the isolation of Phe a, whereas 30°C was used for all other pigments. Prior to this second isolation, chlorophyll a (Chl a) was converted to Phe a (magnesium removal) by 2 M HCl, extracted by *n*-hexane and dried under a cold stream of argon.

The chlorins studied were identified by comparison with published UV-VIS spectra and relative retention times. The range of recorded wavelengths of the DAD spectra was set to 250-800 nm. Chl a, pheophytin a (Phe a), pyropheophytin a (PPhe a), 13²,17³-cyclopheophorbide-*a*-enol (CPhe a) were quantified by the DAD signal recorded at 660 nm on the basis of calibrations between the DAD signal and spectrophotometric extinction using standard compounds (Nakajima et al., 2003).

After pyridine removal by liquid-liquid extraction with a *n*-hexane-MilliQ bilayer (1:1; v: v), samples were transferred to pre-cleaned tin cups by dichloromethane which was then carefully dried at 35°C. $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values of pigments were analysed on a modified FlashEA1112 Automatic Elemental Analyser connected to a Thermo Finnigan Delta plus XP isotope ratio mass spectrometer via a ConFlo III (Ogawa et al., 2010). The $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values are reported relative to Vienna PeeDee Belemnite (VPDB) and to atmospheric N₂ (AIR), respectively. The analytical errors were within 0.4 and 0.8‰ for $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values, respectively, based on repeated analysis of our laboratory standard (Nickel octaethylporphyrin: $\delta^{13}\text{C} = -34.17 \pm 0.06$ ‰, $\delta^{15}\text{N} = 0.86 \pm 0.03$ ‰).

Isotopic fractionation factors were expressed in the epsilon notation with $^{13}\epsilon_{a/b}$ values corresponding to $^{13}\epsilon_{a/b} = 1000 [({}^{13}\text{C}/{}^{12}\text{C})_a / ({}^{13}\text{C}/{}^{12}\text{C})_b - 1]$ and $^{15}\epsilon_{a/b}$ values to $^{15}\epsilon_{a/b} = 1000 [({}^{15}\text{N}/{}^{14}\text{N})_a / ({}^{15}\text{N}/{}^{14}\text{N})_b - 1]$.

2.5. Radiocarbon analyses

The radiocarbon (^{14}C) content of the bulk TOC was analysed after removal of inorganic carbon from the sediment samples with 10% HCl (1h at 60 °C and 10 h at room temperature). The HCl was removed by repeated washing with Milli-Q water. The dried sediment samples were converted to graphite-cathodes using standard methods described by Rethemeyer et al. (2013). AMS ^{14}C analysis was performed at the CologneAMS facility, Germany. Results are reported in fMC with 1 sigma measurement uncertainty.

3. Results

3.1. Bulk parameters

The total organic carbon (TOC) ranged between 1.8 and 3.8 wt% in the laminated part of the sediment core (upper 40 cm, corresponding to ca. 1896-2009), with a slight increase towards the surface within the upper 17 cm (since ca. 1952; Fig. 2a). In contrast, the total inorganic carbon (TIC) concentration increased from 6.5 wt% at 33-34 cm (ca. 1910-1913) to the maximum value of 9.5 wt% at 17-18 cm (ca. 1948-1952), then ranging between 7.5 and 8.8 wt% in the upper 15 cm (since ca. 1959; Fig. 2b). The total nitrogen (TN) remained almost constant with ca. 0.3 wt% in the lower part of the profile before increasing from ca. 14 cm (ca. 1963) to 0.6 wt% in the surface sediment (ca. 2005-2009; Fig. 2c)

Bulk sediment molar C/N ratios ranged between 6 and 8 throughout the core (Fig. 2d). $\delta^{13}\text{C}$ values of the organic carbon ($\delta^{13}\text{C}_{\text{org}}$) ranged between -34.5 and -29.7‰, with a constant decrease from -30.6 to -34.5‰ between 10-11 cm (ca. 1973-1977) and the surface sediment (Fig. 2e). Bulk $\delta^{15}\text{N}$ values increased from 4.9 to 6.7‰ between 37-

38 cm (ca. 1900-1901) and 32-33 cm (ca. 1913-1916), respectively, but remained between 6.1 and 6.9‰ throughout the upper laminated part of the core (0-25 cm; since ca. 1919; Fig. 2f).

The average C/N ratio, $\delta^{13}\text{C}_{\text{org}}$ and TN concentration of the turbidite section between 25 and 31 cm (1918) was very similar to the laminated sections with values of 7.7, -30.6‰ and 0.2 wt%, whereas the TOC, TIC and $\delta^{15}\text{N}$ values were lower with values of 1.5 wt%, 6.4 wt% and 4.7‰ (Fig. 2).

Radiocarbon (^{14}C) analyses of the uppermost three sediment samples (0-6 cm) revealed ages between 1290 ± 40 and 1740 ± 40 years before present (yr BP) in 2-4 cm and 0-2 cm, respectively (Table 1). The fraction of bomb corrected ^{14}C relative to modern levels (fMC) ranged between 0.805 ± 0.004 and 0.852 ± 0.004 in 2-4 cm and 0-2 cm, respectively (Table 1).

3.2. Chlorin distributions

The chlorin distributions in the Lake Zurich sediments were dominated by chlorophyll *a* (Chl *a*) and its derivatives; pheophytin *a* (Phe *a*), Phe *a* epimer, pyropheophytin *a* (PPhe *a*), $13^2,17^3$ -cyclopheophorbide-*a*-enol (CPhe *a*), chlorophyllone *a* (Chlone *a*) as well as steryl and carotenol chlorin esters (SCEs and CCEs, respectively), which were detected in all samples of the core (Fig. 3).

Both Chl *a* and Phe *a* concentrations first decreased from 1.1 and 1.5 mg g⁻¹ TOC at 37-40 cm (ca. 1900-1907), respectively, until 20-22 cm (ca. 1933-1942), before increasing to 1.6 and 1.3 mg g⁻¹ TOC at 4-6 cm (ca. 1989-1996; Fig. 4a). Towards the sediment surface, the concentrations of both pigments decreased progressively. In contrast, PPhe *a* remained relatively constant throughout the profile (0.2-0.4 mg g⁻¹ TOC), with lowest values in the surface sediment. The concentration of CPhe *a*

increased from 0.2 to 0.5 mg g⁻¹ TOC in 37-40 cm (ca. 1900-1907) and 4-6 cm (ca. 1989-1996), respectively, and was higher within the upper 4 cm of the core (0.9-1.2 mg g⁻¹ TOC; ca. 1996-2010; Fig. 4a).

The ratios of Phe *a* to Chl *a*, Pphe *a* to Chl *a* and Pphe *a* to Phe *a* showed similar trends, increasing from the lowermost sample to a maximum of 2.2 at 24-26 cm (ca. 1919-1926), 1.0 at 20-22 cm (ca. 1933-1942), and 0.5 at both 8-10 cm (ca. 1978-1983) and 20-22 cm (ca. 1933-1942), respectively, then decreasing towards the sediment surface (Fig. 4c). All ratios are again slightly higher close to the sediment surface.

Apart from intermediate values (0.6) between 4 and 7 cm (ca. 1984-1994) as well as at 34-35 cm (ca. 1906-1910), the high chlorin index throughout the core (≥ 0.7) suggests a high degree of degradation of chlorophylls throughout the core (Fig. 4c). The Phe *a* to Chl *a* ratios resemble approximately the trends of the chlorin index (Fig. 4c). The total chlorin concentration profile (determined by fluorometry using a Chl *a* standard based external calibration curve; Schubert et al., 2005) also resembles approximately the profiles of single pigments (i.e. Chl *a* and Phe *a*) and the sum of Chl *a*, Phe *a*, Pphe *a* and CPhe *a* (Figs. 4a, 4b). These profiles show that the concentrations of the chlorins were highest in sediment depths characterised with a low degree of chlorin degradation (Figs. 4a, 4b, 4c).

3.3 *Compound-specific carbon and nitrogen isotopic compositions of sedimentary chlorins*

The measured molar carbon to nitrogen (C/N) ratios of most isolated compounds (Chl *a*, Phe *a* and Pphe *a*) agreed within 10% with predicted molar C/N ratios of 13.8 for Chl *a* and Phe *a*, 13.3 for Pphe *a* and 8.0 for CPhe *a* (Table 2) based on their

chemical structure. In contrast, measured molar C/N ratios of Chl *a* fraction in 0-2 cm (2002-2010), 8-10 cm (ca. 1978-1983) and 20-22 cm (ca. 1933-1942) with values of 22.4, 18.0 and 17.2, respectively, were higher than theoretical predictions (Table 2). Such a high value may be explained by contamination of lipids that cannot be removed even after the dual HPLC processes (Tyler et al., 2010).

The $\delta^{13}\text{C}$ values of Chl *a*, Phe *a* and PPhe *a* ($\delta^{13}\text{C}_{\text{Chl-}a}$, $\delta^{13}\text{C}_{\text{Phe-}a}$ and $\delta^{13}\text{C}_{\text{PPhe-}a}$, respectively) ranged between -35.1 and -30.2‰ (Fig. 5a). The highest values were -31.8‰ for Chl *a* at 24-26 cm (ca. 1919-1926), -32.5‰ for Phe *a* at 8-10 cm (ca. 1978-1983), and -30.2‰ for PPhe *a* at 8-10 cm (ca. 1978-1983) depth. After a lowest value of ca. -35‰ for Chl *a* and Phe *a* at 4-6 cm (ca. 1989-1996), their $\delta^{13}\text{C}$ values increased towards the sediment surface, whereas $\delta^{13}\text{C}$ values of PPhe *a* decreased progressively to -33.6‰ at 2-4 cm (ca. 1996-2002) (Fig. 5a).

The $\delta^{15}\text{N}$ values of Chl *a*, Phe *a* and PPhe *a* ($\delta^{15}\text{N}_{\text{Chl-}a}$, $\delta^{15}\text{N}_{\text{Phe-}a}$ and $\delta^{15}\text{N}_{\text{PPhe-}a}$, respectively) ranged between -3.4 and 2.8‰ (Fig. 5b). After an increase in $\delta^{15}\text{N}$ values of all three compounds in the lower part of the core, PPhe *a* increased further and Phe *a* slightly decreased towards the surface sediment. While the $\delta^{15}\text{N}$ values of Chl *a* ranged between -0.1 and 2.3‰ in the 4-22 cm core interval (ca. 1933-1996), values were lower (-3.4 to -1.8‰) between 4 cm and the sediment surface (ca. 1996-2010; Fig. 5b).

4. Discussion

The sediment is characterised by relatively low $\delta^{13}\text{C}$ values of chlorins (-35.1 to -30.2‰). Because the photochemical degradation of Chl *a* in the terrestrial environment during the senescence and death of plant leaves leads to the opening of the tetrapyrrole ring (Matile et al., 1996), the majority of the chlorins, especially Chl *a*,

in the sediment should originate from aquatic sources. This consideration is supported by low bulk C/N ratios (<10) and low $\delta^{13}\text{C}_{\text{org}}$ values (-35.1 to -30.2‰) throughout the core (Fig. 2d, 2e). Thus, the phytoplankton communities could assimilate a ^{13}C -depleted substrate.

The ^{13}C -depleted organic carbon is induced by the eutrophication resulting from the rapid human population growth around the lake in this period (Bossard et al., 2001; Friedrich et al., 2014; North et al., 2014; Posch et al., 2012; Schanz and Thomas, 1981). Although $\delta^{13}\text{C}_{\text{Phe-a}}$ and $\delta^{13}\text{C}_{\text{PPhe-a}}$ values showed some variations through time, their highest values (-30.2‰ and -32.5‰, respectively; Fig. 5a) are observed around 1980, a period corresponding to the eutrophication maximum (Bossard et al., 2001; Posch et al., 2012).

In contrast, relatively low $\delta^{13}\text{C}$ values of all pigments in 1989-2010 may be due to the decreasing productivity and reoligotrophication since the 1980s (Bossard et al., 2001; Schanz and Thomas, 1981). This is in agreement with the decreasing $\delta^{13}\text{C}_{\text{org}}$ values in the upper sediment (Fig. 2). Although the $\delta^{13}\text{C}_{\text{PPhe-a}}$ value further decreased towards the sediment surface, at least the increasing $\delta^{13}\text{C}_{\text{Chl-a}}$ value in 1989-2010 may have resulted from a gradual enrichment of ^{13}C in dissolved inorganic carbon due to the reoligotrophication of the lake. In contrast, higher contributions of PPhe a from lateral transport of OM would be expected under low productivity conditions, which can explain the observed differences of $\delta^{13}\text{C}_{\text{PPhe-a}}$ values relative to the other chlorins in the upper sediment.

In the early 20th century, the relatively low $\delta^{15}\text{N}_{\text{Chl-a}}$, $\delta^{15}\text{N}_{\text{Phe-a}}$ and $\delta^{15}\text{N}_{\text{PPhe-a}}$ values (ranging -2 to 0‰; Fig. 5b) may reflect the blooms of diatoms (*Tabellaria fenestrata*) and cyanobacteria (mainly *P. rubescens*) (Hasler, 1947; Minder, 1938; Schröter, 1897). Carotenoid distributions also indicate a shift from first diatom blooms towards cyanobacterial blooms by the relative increase of the concentration of oscillaxanthin

(but also myxoxanthophyll, canthaxanthin and echinenone) vs. fucoxanthin (Züllig, 1982; 1989). The fucoxanthin peak in 1896 followed by its progressive decrease (Züllig, 1982; 1989) agrees with the decreasing silica accumulation rates in the sediment (Schelske et al., 1987), indicating that diatom populations have decreased since then, whereas cyanobacteria (and especially *P. rubescens*) have become predominant in the lake (Bossard et al., 2001; Posch et al., 2012).

Nitrate is the main nitrogen substrate for *P. rubescens*, which cannot fix N_2 (Jacquet et al., 2005), whereas diatoms assimilate either ammonium or nitrate. Nitrate in the lake is generally not limited throughout the year (e.g. Bleiker and Schanz, 1997; Bossard et al., 2001; Posch et al., 2012) and therefore could be the predominant nitrogen source of diatoms in the lake. The nitrogen fractionation factor (ϵ) associated with ammonium assimilation is generally $\sim 10\text{‰}$ or larger and therefore higher than that of nitrate with ϵ of $\sim 5\text{‰}$ (Ohkouchi and Takano, 2014; Pennock et al., 1996). The apparent fractionation is smaller in natural environments where the substrate is not limited. In Lake Zurich, nitrate concentrations range from at least 2 up to almost 80 $\mu\text{mol N/L}$, whereas ammonium concentrations are typically low (often $< 2 \mu\text{mol N/L}$) in the upper 100 m of the lake for most of the year, but reach especially during summer concentrations of up to ca. 10 $\mu\text{mol N/L}$ and 140 $\mu\text{mol N/L}$ above and below 100 m, respectively (monitoring data 1972-2006; City of Zurich Water Supply).

Therefore, $\delta^{15}\text{N}$ values of chlorins as low as -2‰ in 1900-1907 (Fig. 5b) indicate that the predominant diatoms and cyanobacteria in these early blooms mainly assimilated nitrate. In the first half of the 20th century, *P. rubescens* appeared regularly (Posch et al., 2012; Züllig, 1982; 1989) and a second phytoplankton productivity maximum between ca. 1920 and 1945 (Minder, 1943; Züllig, 1982) may explain the increasing $\delta^{15}\text{N}$ values of all three chlorins, reaching a maximum of 1.0, 1.2 and 2.1 ‰ for Phe *a*, PPhe *a* and Chl *a*, respectively, in 1933-1942 (Fig. 5b).

During the eutrophication maximum in the 1970s, *P. rubescens* (and also oscillaxanthin) could not be detected (Posch et al., 2012; Züllig, 1982; 1989). Algae adapted to the eutrophic environment were predominant and assimilated nitrate and/or ammonium, leading to the lower $\delta^{15}\text{N}_{\text{Chl-a}}$ value (Fig. 5b). Indeed, the sediment comprises a diatom-rich layer, which is dominated by *Melosira (Aulacoseira) granulata* (e.g. Bleiker and Schanz, 1997; Naeher et al., 2013). This species has been used as an eutrophication indicator in lakes (e.g. Smol and Stoermer, 2010) and its predominance in the Lake Zurich sediment further indicates a large bloom in 1982. Other important and abundant diatom species in the lake include *Stephanodiscus hantzschii*, *Asterionella formosa* and *Fragilaria crotonensis* (Bleiker and Schanz, 1997; Thomas, 1964), which are typical for strong mesotrophic to eutrophic conditions (e.g. Reynolds, 2006), as also observed in other Swiss lakes (e.g. Lotter, 1989; Lotter, 1998).

During blooms, the nitrate pool gets depleted and these diatoms may have assimilated more ammonium, which would lead to a pronounced depletion in ^{15}N and may have resulted in the negative $\delta^{15}\text{N}$ excursion in 1978-1983 (Fig. 5b). Alternatively or concurrently, other cyanobacterial genera in the lake may have increased, including *Microcystis* and *Aphanizomenon*, which are typical for eutrophic lakes (e.g. Beversdorf et al., 2013; Monchamp et al., 2014; Walsby et al., 2006), whereas *P. rubescens* generally appears to be abundant under mesotrophic to oligotrophic conditions (e.g. Reynolds, 1987; Walsby et al., 2006). The progressive increase in eutrophication may have resulted in an increase of *Microcystis* and *Aphanizomenon* relative to *P. rubescens*. Indeed, Züllig (1989) observed that canthaxanthin, a pigment abundant in *Aphanizomenon*, increased during the 1970s, whereas oscilloxanthin was only found in low concentrations at this time, indicating that cyanobacterial communities other than *P. rubescens* increased at that time. In

contrast, diatoms were less abundant at the same time based on continuously decreasing numbers of diatom skeletons within the sedimentary record (Züllig, 1982). While *Microcystis* uses ammonium as nitrogen source, *Aphanizomenon flos-aquae* fixes N₂ during ammonium limitation (Monchamp et al., 2014). Beversdorf et al. (2013) showed that the limitation of ammonium at the end of *Microcystis* blooms in the eutrophic Lake Mendota (Wisconsin, USA) stimulated the increase in *Aphanizomenon* and N₂ fixation. While ammonium assimilation can lead to a strong ¹⁵N-depletion relative to biomass if the substrate is not limited, N₂ fixation is associated either with an enrichment or depletion in ¹⁵N ($^{15}\epsilon_{\text{Chl/biomass}} = -9$ to 9% ; Higgins et al., 2011). Therefore, the increased biomass of *Microcystis* and *Aphanizomenon* associated with higher ammonium assimilation and N₂ fixation rates may also explain the negative shift of $\delta^{15}\text{N}_{\text{Chl-a}}$ value in 1978-1983 (Fig. 5b).

In contrast, the similarity of the $\delta^{15}\text{N}_{\text{Chl-a}}$ value in 1933-1942 and 1989-1996 (Fig. 5b), corresponding to the periods before and after the serious eutrophication, was associated with an elevated biomass of *P. rubescens* (Posch et al., 2012). The elevated production of this cyanobacterium may have resulted in higher nitrate assimilation rates and therefore a shift towards higher $\delta^{15}\text{N}_{\text{Chl-a}}$ values.

The low $\delta^{15}\text{N}_{\text{Chl-a}}$ values in 1996-2010 (-3.4 to -1.8% ; Fig. 5b) coincide with the lake's recent tendency towards oligotrophication and oligomixis. Since the 1970s, phosphate concentration substantially decreased in Lake Zurich, whereas nitrate increased linearly, so the increasing nitrate to phosphorus ratio together with reduced water column mixing were considered to have led to the persistency and predominance of *P. rubescens* in the lake (Posch et al., 2012). Therefore, the enhanced availability of nitrate in the surface water would explain the low $\delta^{15}\text{N}_{\text{Chl-a}}$ value.

In contrast to the low $\delta^{15}\text{N}_{\text{Chl-}a}$ values since ca. 1996, $\delta^{15}\text{N}_{\text{Phe-}a}$ values remained almost constant since the 1930s, whereas $\delta^{15}\text{N}_{\text{PPhe-}a}$ values increased continuously towards the sediment surface (Fig. 5b). These differences may be explained by lateral transport of pre-aged, redeposited chlorins due to sediment focusing in the depocenter of the lake where our sediment was recovered (e.g. Garrett, 1990; Wieland et al., 2001). In addition to the vertical settling of particles, sediment focusing represents an additional lateral component of sediment transport due to the downslope transport of resuspended material together with OM (e.g. Garrett, 1990; Wieland et al., 2001). Therefore, this process also leads to higher sedimentation rates with increasing water depth. Indeed, sediment focusing has also been described for Lake Zurich and was found to be the reason for lateral transport of silicate minerals, carbonate and OM as well as, together with geochemical focusing, for the enrichment of redox sensitive elements such as manganese in the sediments of the deeper lake (Naehrer et al., 2013; Wieland et al., 2001).

Therefore, a higher fraction of the pigments in the surface sediment may not entirely originate from the overlying water column. Particularly, the more degraded Chl *a* derivatives, especially PPhe *a*, could partly originate from post-depositional, in-lake derived, redistributed OM. These chlorins carry isotope records of previous times, resulting in mixed signals in the sediment. The higher $\delta^{15}\text{N}_{\text{Phe-}a}$ and $\delta^{15}\text{N}_{\text{PPhe-}a}$ than $\delta^{15}\text{N}_{\text{Chl-}a}$ values in the upper part of the sediment core could therefore be explained by higher contributions from older, relatively ^{15}N -enriched pigments.

Indeed, the ^{14}C age of the TOC in the uppermost sediment sample (1740 ± 40 yr BP at 0-2 cm) is higher than the sample at 2-4 cm (1290 ± 40 yr BP) and especially higher than the sediment age expected based on varve counting (2002-2010 yr AD), suggesting that the studied sediments also contain older OM. The fraction of modern ^{14}C expressed by the fMC values indicate that the uppermost sample (0-2 cm)

contains about 20%, the two samples below (2-6 cm) about 15% of older TOC, possibly even more if this fraction does not only consists of ^{14}C -dead material. Although the majority of the OM in the lake is of aquatic origin as indicated by low bulk C/N ratios (<10), the high ^{14}C ages and their large offset from the sediment age indicate significant lateral transport within the lake and likely also soil OM. This interpretation is supported by data from Gierga et al. (2016), which demonstrated that pre-aged carbon stored in soils supplied to lakes with small catchments can already lead to large offsets between sediment and ^{14}C age of OM.

Therefore, reduced accumulation rates of OM from the water column can be expected for the recent oligotrophication period relative to the lateral transport of OM, which resulted in the pronounced offsets of $\delta^{15}\text{N}$ values of Chl *a*, Phe *a* and PPhe *a* in the late 1990s to 2010. In line with this interpretation are the higher Phe *a* to Chl *a* ratios together with the higher PPhe *a* concentration in the same period, presumably less affected by *in situ* degradation compared to the older sediments, rather indicating a higher relative degree of laterally transported and redeposited OM.

5. Summary

The $\delta^{13}\text{C}$ values of the sedimentary chlorins and those of bulk OM from Lake Zurich mainly followed the historical trends of eutrophication and reoligotrophication. However, sediment focusing and a lower productivity appear to be the main reasons for the relatively higher contribution of redeposited pigments in the presumably fresher surface sediments of the lake. The $\delta^{15}\text{N}_{\text{Chl-}a}$ values mainly result from nitrate assimilation by the dominating cyanobacterium *P. rubescens* and also follows changes in eutrophication. Furthermore, the $\delta^{15}\text{N}$ values of the chlorins were also affected by phototrophic community assemblage shifts with higher abundances of

diatoms and/or cyanobacteria other than *P. rubescens* (partly utilising ammonium or perform N₂ fixation), especially at the end of the 19th century and during the eutrophication maximum in the 1970s. The low $\delta^{15}\text{N}_{\text{Chl-a}}$ values in the surface sediments reflect the recent oligotrophication trend, characterised by increasing nitrogen to phosphorus ratios and reduced water column mixing, which has been considered to be responsible for the higher persistency and predominance of *P. rubescens* in the lake. The ¹⁴C age of the surface sediments revealed significant contributions of pre-aged, redistributed OM, which also explains the offsets between $\delta^{15}\text{N}$ values of Chl *a* and its pheopigments.

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Figure captions

Fig. 1. Map of Lake Zurich with the coring location at the maximum water depth of 137 m. The contour interval is 50 m. The inset in the upper right shows the map of Switzerland with the location of Lake Zurich.

Fig. 2. Bulk parameters (obtained in core ZH-09-5) plotted vs. age (AD) and depth (cm), including the concentrations of a) total organic carbon (TOC, wt%), b) total inorganic carbon (TIC, wt%), c) total nitrogen (TN, wt%), d) molar

carbon to nitrogen (C/N) ratio, e) carbon isotopic composition of TOC ($\delta^{13}\text{C}_{\text{org}}$, ‰ vs. VPDB) and f) nitrogen isotopic composition of TN ($\delta^{15}\text{N}$, ‰ vs. AIR). The shaded area corresponds to a mass movement deposit (turbidite), interrupting the lamination between 25 and 31 cm of the sediment core and for illustration also the depth scale. The data points in the shaded area represent average values of this turbidite section.

Fig. 3. High performance liquid chromatography - photodiode array detection (HPLC-DAD) chromatograms (660 nm signal) showing pigment distributions analysed in the total lipid extracts from sediments at depths of a) 0-2 cm (ca. 2002-2010; adapted from Naeher et al. (2016) and b) 24-26 cm (ca. 1919-1926) in the cores of Lake Zurich. Abbreviations indicate identified compounds comprising chlorophyll *a* (Chl *a*), pheophytin *a* (Phe *a*), pheophytin *a* epimer (Phe *a* epimer), pyropheophytin *a* (PPhe *a*), 13²,17³-cyclopheophorbide-*a*-enol (CPhe *a*), chlorophyllone *a* (Chlone *a*) and steryl and carotenol chlorin esters (SCEs and CCEs).

Fig. 4. a) Concentrations (mg g^{-1} TOC) of chlorophyll *a* (Chl *a*), pheophytin *a* (Phe *a*), pyropheophytin *a* (PPhe *a*) and 13²,17³-cyclopheophorbide-*a*-enol (CPhe *a*), plotted vs. sediment depth (cm). b) Total chlorin concentrations (mg g^{-1} TOC) analysed by fluorometry according to Schubert et al. (2005) and the sum of the concentrations of Chl *a*, Phe *a*, PPhe *a* and CPhe *a*, plotted vs. age (AD) and sediment depth (cm). c) Chlorin index values (-) and ratios of Phe *a* to Chl *a*, PPhe *a* to Chl *a* and PPhe *a* to Phe *a* plotted vs. age (AD) and sediment depth (cm). c) The depth scale is interrupted because of the turbidite layer between 25 and 31 cm of the sediment.

Fig. 5. a) Carbon ($\delta^{13}\text{C}$, ‰ vs. VPDB) and b) nitrogen ($\delta^{15}\text{N}$, ‰ vs. AIR) isotopic composition of chlorins analysed in the sediments of Lake Zurich, plotted vs. age (AD) and sediment depth (cm). The depth scale is interrupted because of the turbidite layer between 25 and 31 cm of the sediment.

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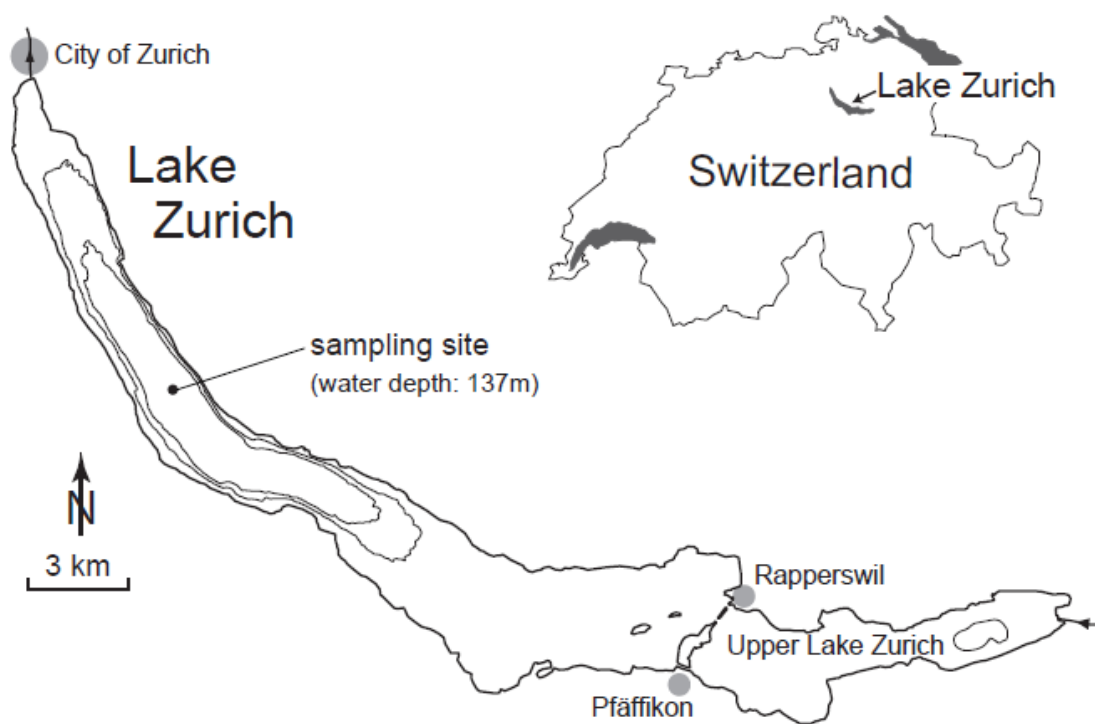


Figure 1

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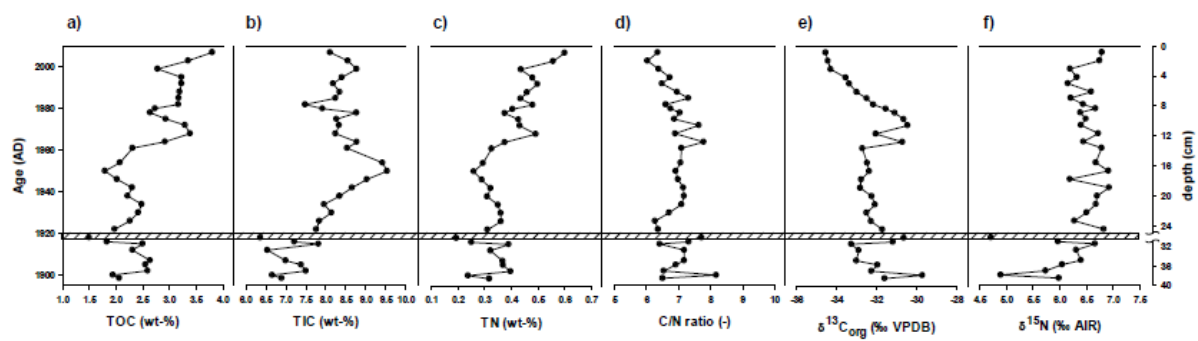


Figure 2

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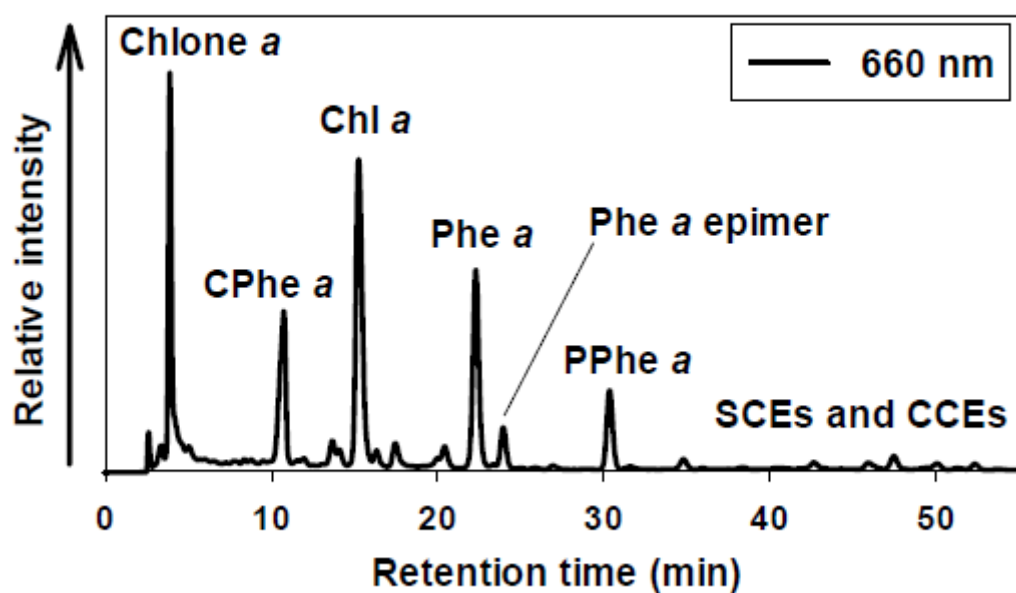
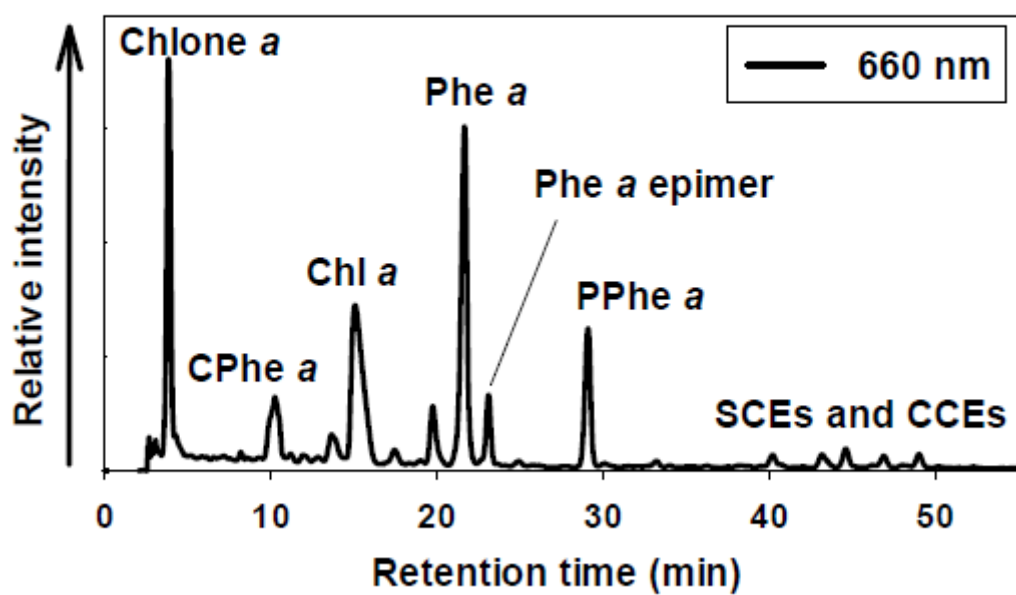
a) 0-2 cm:**b) 24-26 cm:**

Figure 3

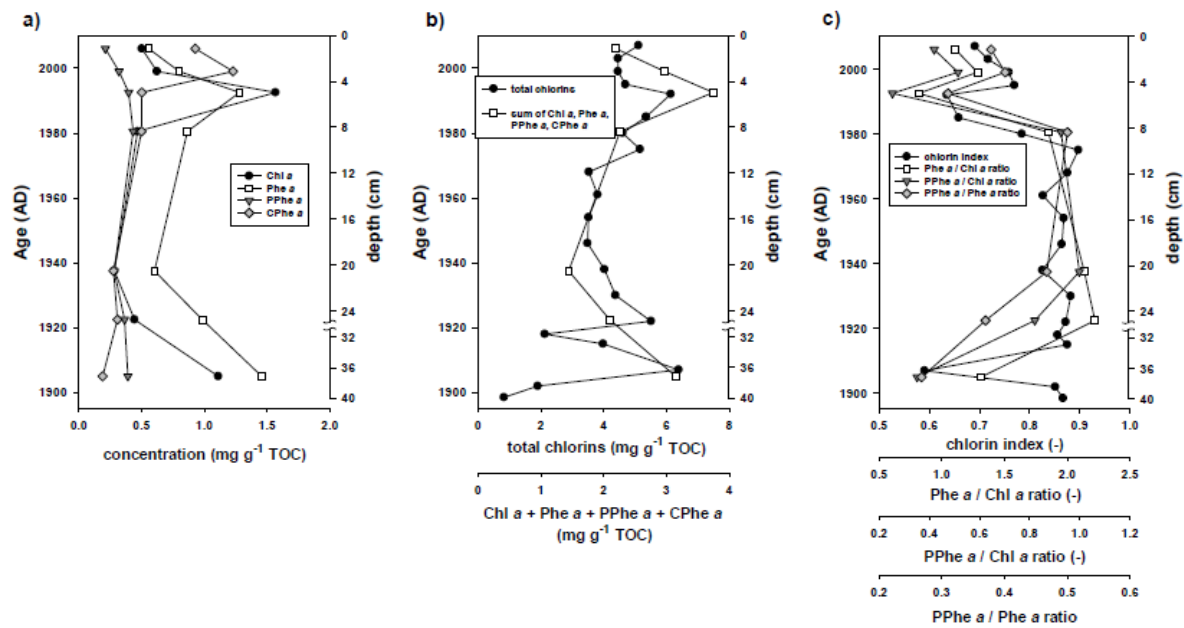


Figure 4

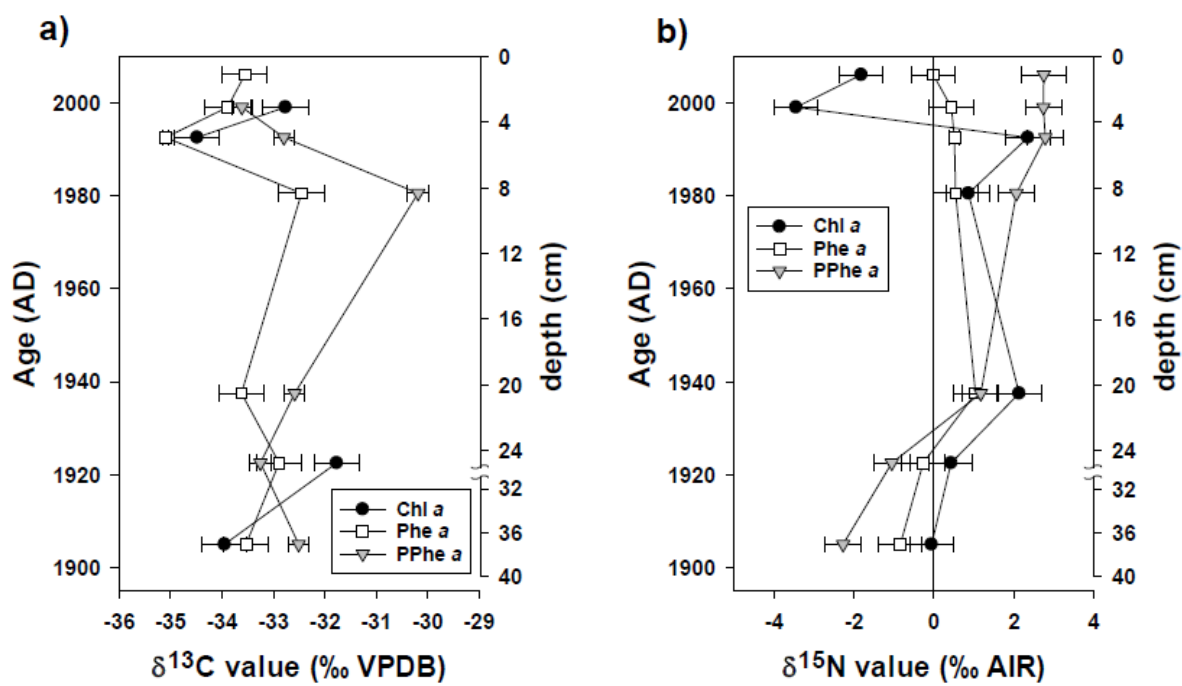


Figure 5

Table 1

Ages of bulk total organic carbon (TOC) determined by radiocarbon analysis (^{14}C age, yr BP) and expected ages of the sediments obtained by varve counting (varve age, yr AD) in core ZH10-18 from Lake Zurich. ^{14}C concentrations are reported in fMC (including normalization to a ^{13}C value of -25‰ and blank correction). Errors are given as 1σ uncertainties.

Sample name	AMS-Lab-ID	depth (cm)	fMC	^{14}C age (yr BP)	Varve age (yr AD)
ZH10-18, 0-2 cm	COL4192.1.1	0.00-0.02	0.805 ± 0.004	1740 ± 40	2002-2010
ZH10-18, 2-4 cm	COL4193.1.1	0.02-0.04	0.852 ± 0.004	1290 ± 40	1996-2002
ZH10-18, 4-6 cm	COL4194.1.1	0.04-0.06	0.842 ± 0.004	1380 ± 40	1989-1996

Table 2

$\delta^{13}\text{C}$ values (‰ vs. VPDB), $\delta^{15}\text{N}$ values (‰ vs. AIR) and measured molar carbon to nitrogen (C/N) ratios of chlorophyll *a* (Chl *a*), pheophytin *a* (Phe *a*) and pyropheophytin *a* (PPh *e a*) in the sediment profile of Lake Zurich. $\delta^{13}\text{C}_{\text{Chl-a}}$ values at 0-2 cm, 8-10 cm and 20-22 cm removed due to high molar C/N ratios (see text for details). Abbreviation: n.d. = not determined.

Depth (cm)	Age (year AD)	Chl <i>a</i>			Phe <i>a</i>			PPh <i>e a</i>		
		$\delta^{13}\text{C}$ (‰ VPDB)	$\delta^{15}\text{N}$ (‰ AIR)	Measured molar C/N ratio (-)	$\delta^{13}\text{C}$ (‰ VPDB)	$\delta^{15}\text{N}$ (‰ AIR)	Measured molar C/N ratio (-)	$\delta^{13}\text{C}$ (‰ VPDB)	$\delta^{15}\text{N}$ (‰ AIR)	Measured molar C/N ratio (-)
0-2	2002-2010		-1.8	22.4	-33.6	0.0	15.1	n.d.	2.7	
2-4	1996-2002	-32.8	-3.4	15.0	-33.9	0.4	14.3	-33.6	2.7	14.4
4-6	1989-1996	-34.5	2.3	15.4	-35.1	0.5	14.1	-32.8	2.8	13.6
8-10	1978-1983		0.9	18.0	-32.5	0.5	14.6	-30.2	2.1	13.8
20-22	1933-1942		2.1	17.2	-33.6	1.0	14.7	-32.6	1.2	14.1
24-26	1919-1926	-31.8	0.4	13.4	-32.9	-0.3	14.5	-33.2	-1.1	14.3
37-41	1900-1907	-33.9	-0.1	14.1	-33.5	-0.8	13.8	-32.5	-2.3	13.2

Highlights

- Pigment distributions reflect rapid pheopigment formation in water column and sediments
- $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values of chlorins follow historical trends of eutrophication and reoligotrophication
- Historical trends in $\delta^{15}\text{N}$ values of chlorins mainly related to population changes of *Planktothrix rubescens*
- $\delta^{15}\text{N}$ offsets of pigments in surface sediment likely due to higher contributions of laterally transported OM

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