Use of sedimentary algal pigment analyses to infer past lake-water total phosphorus concentrations

Simon Belle · Elise Delcamp · L. Jenny Nilsson · Rene Freiberg · G. Peter Appleby · T. Gayane Piliposian · Ilmar Tõnno

Received: 13 October 2021 / Accepted: 6 July 2022 / Published online: 28 July 2022 © The Author(s) 2022

Abstract We tested the feasibility of using sedimentary algal pigment analyses by spectral deconvolution to infer past lake-water total phosphorus concentrations. We established equations that link lake-water nutrient concentrations and sediment pigment concentrations, using a combination of calibration in both space and time, with a training set of 31 Swedish lakes. The calibration dataset yielded a significant positive relationship between total carotenoid concentrations and lake-water total phosphorus concentrations. We also compared sediment-pigment-based nutrient inferences with time series of water column monitoring data to evaluate whether temporal changes in total phosphorus concentrations are well captured by analysis of sedimentary pigments. We found that changes in pigment preservation through time can alter the relationship between concentrations of lake-water nutrients and sedimentary pigments, thus limiting the reliability of historical ecological conditions inferred from pigments in the sediment. Our data suggested that ratios of Chlorophyll derivatives to total carotenoids (CD/TC ratio) and Chlorophyll a to Chlorophyll derivatives (CPI) can be used as proxies for pigment preservation. Using our approach, inferred temporal changes in water-column total phosphorus concentrations in lakes are promising, but require further development, specifically with respect to the influence of pigment degradation in both the water column and sediments, as well as the factors that control such degradation.

Keywords Paleolimnology · Sedimentary pigments · Spectrophotometric analysis · Gauss-peak spectra · Reference conditions · Eutrophication

Introduction

Aquatic ecosystems face tremendous changes as a consequence of a multitude of stressors, including cultural eutrophication, which is a major large-scale driver of ecological change (Schindler 2009). Eutrophication-induced changes have caused degraded ecological status and potential loss of ecological services in lakes worldwide (Wilson and...
The chemical quality of waterbodies is usually assessed by the degree to which present-day conditions (i.e. nutrient concentrations) deviate from those expected in the absence of significant anthropogenic influence, commonly referred to as reference conditions (Bennion and Battarbee 2007). Most environmental monitoring records, however, do not extend beyond the past few decades, and the onset of human impacts on the environment is known to predate substantially the first monitoring data (Dubois et al. 2019), thus making it difficult to assess reference conditions for most freshwater ecosystems. Use of lake sediments as natural archives is therefore a common way to estimate reference conditions in freshwater lakes (Smol 1992). Such sediment records have been shown to provide reliable estimates of past changes in ecological status of lakes, which can be used to set realistic restoration targets (Bennion et al. 2010).

Short-lived primary producers respond rapidly to changes in a wide range of environmental conditions, especially nutrient availability (Anderson et al. 1995). Temporal dynamics of algal biomass and community composition have therefore often been associated with an immediate response to increased nutrient availability (Deshpande et al. 2014; Tõnno et al. 2019). Benthic and pelagic algae contain specific photosynthetic pigments (e.g. chlorophyll a, phaeophytin a, canthaxanthin, etc.) that are archived over extended time-scales in lake sediments, long after the loss of their morphological structure (Cohen 2003). Sedimentary pigment composition, ratios and presence/absence of certain marker pigments can therefore be used to identify past changes in phytoplankton community composition and biomass (Leavitt and Hodgson 2002). The relative concentrations of pigments in lake sediments are therefore a reliable proxy for primary productivity (Reuss et al. 2010) and enable inferences about past changes in nutrient availability in lakes (Guilizzoni et al. 2011). Numerous methods have been developed to quantify the relative concentrations of sedimentary pigments (Leavitt and Hodgson 2002). Spectrophotometric techniques use absorbance spectra of pigment extracts from the whole visible region and rely on the fact that each pigment has its own specific absorbance spectrum (Küpper et al. 2000). Various numerical methods, such as Gauss-peak spectra methods (Küpper et al. 2007) are also available to deconvolute sedimentary pigment spectra as linear combinations of multiple Gaussian functions that correspond to a known pigment-specific absorbance spectrum (Thrane et al. 2015). These spectrophotometric techniques and spectral deconvolution methods can therefore provide a cost-effective and reliable way to reconstruct past changes in nutrient concentrations in lakes.

The reliability of ecological inferences based on sediment pigment analysis can be influenced by the degree of pigment degradation in the water column and sediments. Indeed, pigment concentrations in sediments and their preservation are known to be influenced, in part, by lake morphometry, algal community composition and environmental conditions (Buchaca and Catalan 2007; Bianchi and Canuel 2011). It is also well known that photo-chemical oxidation in the water column and early diagenesis influence pigment concentrations in sediments (Leavitt 1993). In this context, defining an indicator of pigment preservation is crucial, and it has been suggested that the ratio of chlorophyll derivatives to total carotenoids (CD/TC ratio) provides an indication of pigment preservation, as chlorophyll and carotenoids may degrade at different rates (Guilizzoni et al. 2011). Its reliability is still debated, as variations in CD/TC ratios can also be caused by different proportions of terrestrial and aquatic organic matter in the sediment (Sanger and Gorham 1972; Swain 1985) and/or changes in algal community composition (Mikomägi and Punning 2007). Ratios between Chlorophyll a and Chlorophyll derivatives (the so called Chlorophyll Preservation Index [CPI]) have also been suggested as indicators of the degree of pigment degradation in sediments (Buchaca and Catalan 2007), but further investigations are needed to better assess the reliability of these indicators.

This study tested the use of analyses of algal pigment mixtures by spectral deconvolution to infer past water-column total phosphorus concentrations in lakes. We used a 31 Swedish lakes-training set and established equations that link lake-water phosphorus concentrations and sedimentary pigment concentrations. We then compared these pigment-based nutrient inferences with time series of monitoring data to evaluate whether temporal changes in total phosphorus concentrations were well captured by the analysis.
of sedimentary pigments. We also explored relationships between the origin of organic matter in sediments and ratios between different pigment groups as a proxy of pigment preservation.

Study sites

Thirty-one small (29–863 ha) and deep (z_{max} 15.4–47.0 m) Swedish lakes, with relatively small catchments (1.31–57.3 km^2) were selected for this study (Table 1). The lakes display a broad range of limnological characteristics with respect to light penetration (Secchi depth 1.5–11.0 m), Total Organic Carbon concentration (1.76–19.7 mg L^{-1}), light absorbance at 420 nm (0.01 to 0.51), and total phosphorus concentration (2.5–37.8 µg L^{-1}; Table 1), thus enabling study of the relationships between environmental conditions and sedimentary pigments.

Materials and methods

Sediment sampling

In June–July 2020, sediment–water interface cores were retrieved from the deepest point in each lake, using a 9-cm-diameter UWITEC gravity corer. All sediment cores were then split in half lengthwise and the uppermost 1-cm-thick sediment layer in each core was collected immediately and stored at −20 °C until further analyses.

Sediment cores were dated by ^{210}Pb and ^{137}Cs at Liverpool University’s Environmental Radioactivity Laboratory. Sub-samples were analysed for ^{210}Pb, ^{226}Ra, and ^{137}Cs by direct gamma assay, using Ortec HPGe GWL series well-type coaxial low background intrinsic germanium detectors (Appleby et al. 1986). ^{210}Pb was determined via its gamma emissions at 46.5 keV, and ^{226}Ra by the 295 keV and 352 keV γ-rays emitted by its daughter radionuclide ^{214}Pb, following 3 weeks storage in sealed containers to allow radioactive equilibration. ^{137}Cs was measured by its emissions at 662 keV. The absolute efficiencies of the detectors were determined using calibrated sources and sediment samples of known activity. Corrections were made for the effect of self-absorption of low-energy γ-rays within the sample (Appleby et al. 1991). Dates were calculated using the CRS model (Appleby and Oldfield 1978). Discrepancies with any clearly defined ^{137}Cs dates were resolved using the methods outlined in Appleby (2001). The results are presented in Electronic Supplementary Material [ESM] Figs. S1 and S2.

Among the 31 lakes, sediment cores from Lakes Drevviken and Gyltigesjön were selected for further analysis that was designed to compare sedimentary pigment-based nutrient inferences with time series of monitoring data. The two lakes were chosen because they displayed the highest sedimentation rates in the training set. This made them suitable to test whether temporal changes in water column total phosphorus concentrations, observed in time series of monitoring data, can be well captured by quantification of sedimentary pigments. Sediment cores from Lakes Drevviken and Gyltigesjön were sectioned at 1-cm intervals to depths of 30 and 50 cm, respectively.

Environmental data

Monthly mean water quality data during the summer period were retrieved from the Swedish National Monitoring Program database (https://miljodata.slu.se/mvm/). Variables obtained included light absorbance at 420 nm, conductivity, pH, Secchi depth, and calcium, magnesium, total chlorophyll, total organic carbon, nutrient and oxygen concentrations. Since the uppermost sediment layers represent several years of accumulation, mean values for all environmental variables were calculated for the last five available years. Average values are presented in Table 1. Time series of monitoring data were also averaged to match the respective time frames covered by each sediment sample.

Sediment and pigment analysis

Sediment layers were analysed for organic matter concentration (OM, loss-on-ignition as % of dry mass). To estimate the relative contribution of terrestrial and aquatic organic matter to the total sediment organic matter, samples were analysed for carbon and nitrogen concentration and C/N weight ratios at the SLU Stable Isotope Laboratory (Umeå, Sweden). Sedimentary pigments were analysed following modified methods of Leavitt and Hodgson (2002), Guilizzoni et al. (2011) and Thrane et al. (2015). Briefly, sediment samples were thawed in the dark at 4 °C overnight. Then, ~1 g of fresh sediment was extracted...
Table 1 Physical and chemical characteristics of the 31 lakes in the training set

| Lake Core | WS(km²) | Depth(m) | Area(km²) | Abs420 | Ca | Chl | Cond25 | Mg | NH4N | NO2 | NO3 | pH | TOC | Tot_P | Tot_N | Secchi |
|-----------|---------|----------|-----------|--------|----|-----|--------|----|------|-----|-----|----|-----|-------|-------|--------|
| Bleklången BLA_20d_P1a | 18.76 | 17.5 | 1.81 | 0.16 | 3.8 | 5.3 | 4.4 | 1.1 | 18.7 | 66.7 | 6.6 | 14.2 | 10.8 | 479 | 2.2 |
| Bysjön BYS_20b_P1b | 38.90 | 20.5 | 5.05 | 0.15 | 3.4 | 2.7 | 3.4 | 0.9 | 15.1 | 61.0 | 6.7 | 9.3 | 7.7 | 250 | 3.4 |
| Drevsöken Dre_20d_P1b | 35.72 | 15.4 | 5.28 | 0.04 | 30.6 | 20.8 | 352 | 4.8 | 278.2 | 3.6 | 7.9 | 9.2 | 378 | 568 | 1.8 |
| Fågelnäs FOR_20_P2a | 10.37 | 21.0 | 1.56 | 0.10 | 4.8 | 23 | 4.9 | 0.8 | 10.5 | 9.4 | 7.2 | 6.2 | 5.8 | 362 | 4.1 |
| Glumslöv GLL-20_P1a | 12.16 | 31.5 | 1.62 | 0.03 | 10.5 | 39.7 | 11 | 0.8 | 29.1 | 21.8 | 6.7 | 9.5 | 3.7 | 290 | 4.1 |
| Granösjön Gra_20c_P1a | 10.41 | 21.6 | 0.45 | 0.11 | 3.4 | 2.2 | 3.4 | 0.9 | 11.3 | 29.1 | 6.7 | 9.5 | 3.7 | 290 | 4.1 |
| Gyltigesjön GYL_20_P2a | 6.87 | 21.6 | 0.39 | 0.51 | 5.1 | 3.2 | 3.2 | 0.9 | 12.2 | 27.0 | 6.5 | 9.3 | 7.7 | 250 | 3.4 |
| Haggen HAG_20b_P1a | 47.47 | 29.0 | 8.63 | 0.13 | 3.2 | 3.5 | 3.4 | 0.8 | 12.5 | 91.4 | 6.8 | 8.3 | 8.9 | 270 | 3.4 |
| Hällvattnet HAL_20c_P1b | 43.48 | 47.0 | 6.57 | 0.13 | 3.4 | 2.7 | 3.4 | 0.9 | 11.1 | 27.0 | 6.5 | 9.3 | 7.7 | 250 | 3.4 |
| Hökesjön HOK_20_P1b | 40.32 | 22.0 | 0.51 | 0.02 | 4.0 | 29 | 4.6 | 0.9 | 12.2 | 37.5 | 7.0 | 5.2 | 3.6 | 261 | 6.7 |
| Holmeshultasjön HOL_20_P2a | 5.75 | 16.5 | 0.64 | 0.10 | 4.8 | 4.0 | 6.4 | 1.8 | 278.2 | 3.6 | 7.9 | 9.2 | 378 | 568 | 1.8 |
| Lagmanshagasjön LAG_20_P1b | 38.13 | 17.0 | 2.95 | 0.04 | 6.3 | 3.7 | 6.4 | 1.2 | 33.0 | 188.0 | 6.9 | 10.1 | 7.0 | 254 | 3.3 |
| Långsjön LAN_20_P1b | 10.11 | 20.5 | 0.64 | 0.23 | 8.0 | 11.0 | 9.4 | 0.8 | 10.0 | 10.0 | 6.9 | 10.1 | 7.0 | 254 | 3.3 |
| Linnestadsjön LIN_20_P1b | 19.75 | 23.5 | 2.85 | 0.19 | 4.4 | 4.1 | 5.7 | 1.2 | 13.3 | 160.8 | 6.7 | 9.9 | 7.0 | 410 | 2.5 |
| Lilla Öresjön LIL_20_P1b | 4.73 | 17.2 | 0.64 | 0.13 | 1.2 | 2.3 | 2.2 | 0.7 | 22.0 | 65.6 | 5.8 | 10.2 | 6.6 | 121 | 2.1 |
| Majsjön MAJ_20_P1b | 19.75 | 21.5 | 2.85 | 0.19 | 4.4 | 4.1 | 5.7 | 1.2 | 13.3 | 160.8 | 6.7 | 9.9 | 7.0 | 410 | 2.5 |
| Munksjön MUN_20_P2a | 2.40 | 20.4 | 0.84 | 0.18 | 19.5 | 18.9 | 21.6 | 3.3 | 75.7 | 81.2 | 75 | 9 | 7.0 | 260 | 1.5 |
| Norra Vallsjön NOR_20_P1b | 10.37 | 29.2 | 1.4 | 0.07 | 8.0 | 11.0 | 9.4 | 0.8 | 10.0 | 10.0 | 6.9 | 10.1 | 7.0 | 254 | 3.3 |
| Övre Skärsjön OSK_20b_P1a | 8.77 | 32.0 | 1.7 | 0.07 | 8.0 | 11.0 | 9.4 | 0.8 | 10.0 | 10.0 | 6.9 | 10.1 | 7.0 | 254 | 3.3 |
| Örvattnet OVR_20_P1a | 2.30 | 21.3 | 0.4 | 0.03 | 2.4 | 1.5 | 2.8 | 0.7 | 24.2 | 42.5 | 6.6 | 4.4 | 5.8 | 329 | 2.2 |
| Täftesträsket TAF_20c_P1b | 12.20 | 17.5 | 2.22 | 0.13 | 2.7 | 5.7 | 3.0 | 0.7 | 27.0 | 47.0 | 6.8 | 9.3 | 7.7 | 250 | 3.4 |
| Torrgårdsvatten TOR_20_P1b | 57.30 | 29.2 | 0.49 | 0.04 | 2.7 | 5.7 | 3.8 | 0.7 | 19.0 | 24.7 | 6.6 | 4.4 | 5.8 | 329 | 2.2 |
| Tryssjön TRY_20_P1b | 12.21 | 19.6 | 0.29 | 0.12 | 2.7 | 5.7 | 3.0 | 0.7 | 27.0 | 47.0 | 6.8 | 9.3 | 7.7 | 250 | 3.4 |
| V.-Rännöbodsjön VAS_20c_P1a | 4.56 | 19.5 | 0.46 | 0.11 | 3.3 | 5.5 | 4.7 | 1.2 | 12.3 | 75.2 | 6.9 | 8.2 | 9.8 | 260 | 1.5 |
| Västra Skälsjön VSK_20b_P1b | 1.31 | 19.0 | 0.43 | 0.03 | 2.9 | 1.7 | 2.9 | 0.7 | 22.0 | 65.6 | 5.8 | 10.2 | 6.6 | 121 | 2.1 |

Abbreviations for variables include: WS(km²) – watershed size; Depth(m) – maximum lake depth; Area(km²) – lake area; Abs420 – absorbance at 420 nm; Chl – total chlorophyll concentration; Cond25 – specific conductance at 25 °C; TOC – total organic carbon concentration; Tot_P – total phosphorus concentration; Tot_N – total nitrogen concentration. Data are reported from [https://miljodata.statu.se/mvm/](https://miljodata.statu.se/mvm/).
with 10 mL 90% acetone in 50-mL centrifuge tubes. Tubes were flushed using nitrogen gas to ensure a full evacuation of ambient air, and tubes were then fully homogenized by using a vortex mixer (1 min), and then centrifuged (10 min, 3500 rpm). The mixture was stored in the freezer (-20 °C) overnight (12 h). On the following day, 3 mL of pigment extract was analysed with a UV–VIS spectrophotometer (Lambda 365) at 0.1-nm steps and with a spectral bandwidth of 1 nm in a 1-cm (optical path) UV micro-Cuvette. Measurements were performed in triplicate (i.e. each wavelength was measured 3 times), and average values were calculated and used for further analyses.

Data analysis

Principal component (PC) analysis was applied to the standardized (data scale to zero) lake water chemical characteristics, followed by a canonical correspondence analysis to assess whether lake morphometry (lake area and maximum depth) and catchment area could be associated with existing environmental gradients. Relative concentrations of individual sediment pigments were evaluated by spectral deconvolution using a modified Gauss-peak method developed by Thrane et al. (2015). Pigment concentrations were expressed as nanomoles per gram (dry mass) of sediment organic matter (nmol g⁻¹ OM). Individual pigments were then pooled into main pigment groups: total carotenoids (TC) and chlorophyll derivatives (CD), and their ratios were calculated as indicators of pigment preservation in sediments. We also calculated the Chlorophyll Preservation Index (CPI) as the ratio between Chlorophyll a and the sum of Chlorophyll a and Pheophytin a (Buchaca and Catalan 2007). Data transformations were applied to stabilize the variance and generalized additive models were used to link relative concentrations of the main pigment groups to nutrient water concentrations. Because high CD/TC ratios can indicate poor pigment preservation, we tested a second model that excludes samples with the highest CD/TC ratios. To evaluate how well temporal changes in total phosphorus water concentrations can be captured by the analysis of sedimentary pigments, pigment-based inferences of phosphorus concentrations were also compared to time series of observed nutrient concentrations using generalized additive models. All statistical analyses were performed and plots constructed using the R 4.1.1 software (R Core Team 2021).

Results

Calibration dataset

The first two PC axes of the standardized lake water chemical characteristics accounted for 47.5% and 19.9% of the variance, respectively (Fig. 1A). The PC1 axis explained nutrient concentrations and associated variables such as total phosphorus, pH and conductivity, with negative PC1-values representing nutrient-rich lakes (Fig. 1B). The PC2 axis instead represented variables that reflected water transparency, such as light absorbance at 420 nm and Secchi depth, with positive values representing humic lakes. In our 31-lake calibration dataset, lakes were mainly distributed along the gradient in light penetration (PC2 axis, Fig. 1B). Furthermore, none of the tested explanatory variables (maximum water depth, lake size and catchment area) known to have influence on sedimentary pigment preservation (Buchaca and Catalan 2007) showed significant association with observed environmental gradients.

Pigment concentrations in lake sediments

Total carotenoid (TC) values ranged from 0.16 to 18 nmol g⁻¹ OM and CD/TC ratios ranged from 2.72 to 71.35 (Fig. 2A). Overall, the highest CD/TC ratios were strongly associated with low TC values (Fig. 2A). A strong positive relationship (R² = 0.48, p-value < 0.001) was found between total phosphorus concentrations and TC values (Fig. 2B and Table 2), and samples with the highest CD/TC ratios clearly did not follow the observed trend (red dots in Fig. 2B). After excluding these samples (n = 15), the performance of the model linking total phosphorus concentrations in water to TC values was significantly improved (R² = 0.88, p-value < 0.001; Fig. 2C and Table 2). Significant correlation was found between CPI and CD/TC ratios (R² = 0.51, p-value < 0.001, Fig. 3A). No correlation was found between CD/TC ratios and oxygen concentrations (Fig. 3B) whereas CD/TC ratios were positively correlated to maximum lake water depth (R² = 0.45, p-value < 0.001, Fig. 3C).
Fig. 1 A Factorial map of principal component analyses (PC1 vs. PC2) performed on standardized lake water chemistry characteristics. B Correlation circle representing variable contributions to the first two PC-axes.
Photosynthetic pigments were also quantified in the 30 sediment layers from the Lake Drevviken sediment core. Monitoring data over the study period showed similar temporal dynamics in total phosphorus and Chlorophyll $a$ water concentration, with a dramatic decrease between 1982 and 2002 (Fig. 4A), and we therefore expected to observe a similar decreasing pattern in sedimentary pigments. In the Lake Drevviken sediment core, TC values ranged from 12.45 to 22.56 nmol g$^{-1}$ OM (Fig. 4B), whereas CD/TC ratios ranged from 3.58 to 6.6 (Fig. 4C). Temporal changes in CD/TC ratios revealed a decreasing trend from 1975 to 2002 (from 30 to 19 cm depth in the core) and values thereafter remained stable to the top. From
1975 to 2002, a period that showed a decline in total phosphorus and Chlorophyll $a$ water concentrations, but also higher CD/TC ratios, TC values remained unexpectedly stable. When including all pigment samples, the relationship between total phosphorus concentrations in the water column and pigment samples was unexpectedly negative, but also strongly influenced by samples with the highest CD/TC ratios (Fig. 5B). After excluding those samples, high TC values were associated with high total phosphorus concentrations in the water (Fig. 5C), but because of the absence of significant temporal trends in water-column total phosphorus concentrations during the period (from 2002 onwards; Fig. 4C), the relationship between these variables cannot be further explored.

Photosynthetic pigments were also quantified in 50 sediment layers from the Lake Gyltigesjön sediment core. TC values range from 0.7 to 4.99 nmol g$^{-1}$ OM (Fig. 6B), whereas CD/TC ratios mainly range from 7.5 to 13.3, except for one sample with a CD/TC ratio of 38.4 (Fig. 6C). TC values increased from 34 to 10 cm depth in the core whereas CD/TC ratios instead showed no significant trend. At sediment depths $>10$ cm, TC values decreased, whereas CD/TC ratios increased. There was no significant relationship between CD/TC ratios and TC (Fig. 6A). Because of large discrepancies between $^{210}$Pb dates calculated using the CRS model and $^{137}$Cs/$^{241}$Am records (ESM Fig. S2), the Lake Gyltigesjön sediment core could not be dated reliably and sediment variables could only be plotted against depth in the core. Correlation between sediment and water-column monitoring data was not possible.
C/N weight ratios ranged between 8.5 and 9.5, and 17 and 20 for Lakes Drevviken and Gyltigesjön, respectively (Fig. 7). No temporal trend was observed in the Lake Drevviken sediment core, whereas a small increase in C/N weight ratios was seen in the uppermost samples from Lake Gyltigesjön. No significant relationship was found between CD/TC ratios and C/N weight ratios for the entire 31-lake dataset, or for the Lake Drevviken and Lake Gyltigesjön samples, analyzed separately (Fig. 7). However, sediment samples from Lake Drevviken displayed low C/N weight ratios (higher proportion of aquatic organic matter) and low CD/TC ratios (Fig. 7), whereas Lake Gyltigesjön showed the opposite pattern.

Samples with the highest CD/TC ratios were marked with red dots. Phosphorus data were log-transformed to stabilize the variance. Differences in point numbers between panels A and B are a consequence of shorter time series of monitoring data than those for sediment-based inferences.
Discussion

We examined the relationship between sedimentary pigment and water-column total phosphorus concentrations in Swedish lakes, and found that total carotenoid concentrations in sediments were strongly influenced by total phosphorus concentrations in the water. We suggest, however, that pigment degradation in both the water column and sediments often disrupts the link between lake-water nutrient concentrations and sedimentary pigments, potentially limiting the reliability of pigment-based trophic status inferences from downcore pigment values.

Using PC analysis, we found that the study lakes were mainly distributed along a light penetration gradient (PC2), whereas nutrient concentrations and associated variables contributed very little to this main gradient, thus limiting the influence of the light penetration gradient on the link between sediment pigment concentrations and water-column nutrients. Furthermore, pigment concentrations in sediments and their preservation are known to be influenced partially by lake morphometry (Buchaca and Catalan 2007) and may therefore induce a bias in trophic state inferences if the gradient in nutrient concentrations was also associated with lake morphometry (e.g., nutrient-rich lakes are also the deepest ones, or vice versa). In our dataset, however, lake morphometry was not associated with any of the lake water chemistry characteristics, thus limiting potential confounding effects.

We used a spectral deconvolution method, applied to spectrophotometer-based absorbance spectra measures, to quantify algal pigment mixtures in lake sediments. We found a significant positive relationship between total carotenoid (TC) concentrations in sediments and lake-water total phosphorus concentrations. Our results also showed that pigment concentrations were higher in sediments with a higher proportion of aquatic organic matter than in sediments with terrestrial-dominated OM (C/N weight ratios are lower in Lake Drevviken sediments than in Lake Gyltigesjön sediments). Our results therefore support previous findings that showed similar patterns in different lake types and regions (Waters et al. 2005; Das et al. 2011; Guilizzoni et al. 2011; Sanchini and Grosjean 2020). Furthermore, the spectral deconvolution approach has also been proven efficient at quantifying sedimentary pigments, in comparison with more time-consuming and expensive approaches such as high-performance liquid chromatography (Thrane et al. 2015; Sanchini and Grosjean 2020). Our study illustrates the potential of quantification of sedimentary algal pigment mixtures by spectral deconvolution, to infer past changes in water-column nutrient concentrations in Swedish lakes.

Our results also showed, in calibrations across both space and time, potential problems with pigment preservation. Indeed, all sediment samples that had TC concentrations that were not positively associated with TP concentrations also showed the highest CD/TC ratios (Figs. 2B and 5B). First, we explored whether this pattern could be caused by differential proportions of terrestrial/aquatic organic matter, since few studies have shown that CD/TC ratios are lower in lake sediments than in terrestrial soils (Sanger and Gorham 1972; Swain 1985). We used C/N weight ratios to estimate the relative contributions of terrestrial and aquatic organic matter to the total sediment organic matter, C/N weight ratios being higher in terrestrial-dominated sediments (Meyer and Ishiwatari 1993). Our results did not corroborate the terrestrial vs. aquatic organic matter hypothesis, as no relationship was found between C/N weight ratios and CD/TC ratios, in neither the lake-specific nor training set levels. Therefore, variations in CD/TC ratios were not mainly associated with changes in organic matter production and/or inputs.

Furthermore, our results showed a strong correlation between CD/TC ratios and the Chlorophyll Preservation Index (CPI), an indicator of pigment preservation in sediments (Buchaca and Catalan 2007;
Deshpande et al. 2014), thus revealing potential confounding problems associated with pigment degradation. Previous studies, however, revealed contradictory findings regarding differential degradation rates between Chlorophyll and carotenoids. Moss (1968) reported that carotenoids degrade faster than chlorophylls under oxidizing conditions, leading to high CD/TC ratios for degraded samples, whereas Leavitt and Hodgson (2002) suggested that chlorophylls are much more susceptible to degradation, compared with carotenoids, and are generally less stable in the environment. According to Moss (1968), our results suggested that high CD/TC ratios indicate lower pigment preservation because of higher degradation of carotenoids. Our study also suggested that photosynthetic pigment degradation occurred in both the water column and sediments, as there was a significant positive correlation between CD/TC ratios and lake water depth, and higher CD/TC ratios were reported at the base of the Lake Drevviken sediment core. Pigment degradation in the water column is a well-described process (Leavitt and Brown 1988; Leavitt 1993), and previous studies revealed that pigment concentrations in sediments can be influenced by lake morphometry (Buchaca and Catalan 2007). Pigment degradation in sediments, however, is still poorly understood (San-chini and Grosjean 2020), and very little is known about how early and late diagenetic processes impact pigment concentrations and the factors that control diagenesis. Interpretations of the CD/TC ratio as a proxy for pigment degradation appear, therefore, to be complex, as its variation often involves multiple mechanisms. Interpretations will improve with a better understanding of pigment degradation in lake water and sediments.

Multiproxy trophic state reconstruction could, however, help to strengthen the reliability of inferences based on sedimentary algal pigment mixtures quantified by spectral deconvolution. For instance, tracking temporal changes in the composition of sediment organic matter (e.g., by means of C/N weight ratio analysis) to rule out shifts in proportions of terrestrial/aquatic organic matter would be an interesting approach. Results of our study suggest that inferring temporal changes in past water-column nutrient concentrations in Swedish lakes using sediment pigment concentrations and ratios is a promising approach, but requires further development, specifically regarding the degree of pigment degradation, as such degradation could limit the reliability of pigment-based ecological inference in paleolimnology.

Acknowledgements This study is part of the CENTURION (Cumulative effects of climate change and eutrophication on Swedish lakes; Grant Number: NV-802-0047-19) project funded by the Swedish Environmental Protection Agency to Simon Belle (SLU). IT and RF were funded by the Estonian Research Council (PRG709 & PRG1167). We thank Jojo Place and Daniel Goedkoop for assistance during fieldwork, and Willem Goedkoop for his comments on an earlier version of this manuscript.

Author contribution SB designed the study. SB and JN collected the samples. AP and PG produced age-depth models. ED and SB analysed samples. SB wrote the paper with substantial contribution from all co-authors.

Funding Open access funding provided by Swedish University of Agricultural Sciences.

Declarations

Competing interest The authors declare that they have no competing interests.

Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if changes were made. The images or other third party material in this article are included in the article’s Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article’s Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this licence, visit http://creativecommons.org/licenses/by/4.0/.

References

Anderson NJ, Renberg I, Segerstrom U (1995) Diatom production responses to the development of early agriculture in a boreal forest lake-catchment (Kassjon, Northern Sweden). J Ecol 83:809. https://doi.org/10.2307/2261418

Appleby PG, Nolan PJ, Gifford DW, Godfrey MJ, Oldfield F, Anderson NJ, Battarbee RW (1986) 210Pb dating by low background gamma counting. Hydrobiol 143:21–27. https://doi.org/10.1007/BF00026640

Appleby PG, Richardson N, Nolan PJ (1991) 241Am dating of lake sediments. Hydrobiol 214:35–42. https://doi.org/10.1007/BF00050929

Bennion H, Battarbee R (2007) The European Union water framework directive: opportunities for palaeolimnology.
Bennion H, Battarbee RW, Sayer CD, Simpson GL, Davidson TA (2010) Defining reference conditions and restoration targets for lake ecosystems using palaeolimnology: a synthesis. J Paleolimn 45:533–544. https://doi.org/10.1007/s10933-010-9419-3

Bianchi TS, Canuel EA (2011) Chemical biomarkers in aquatic ecosystems. Princeton University Press, Princeton NJ

Buchaca T, Catalan J (2007) Factors influencing the variability of pigments in the surface sediments of mountain lakes. Freshw Biol 52:1365–1379. https://doi.org/10.1111/j.1365-2427.2007.01774.x

Clementson LA, Wojtasiewicz B (2019) Dataset on the absorption characteristics of extracted phytoplankton pigments. Data Brief 24:103875. https://doi.org/10.1016/j.dib.2019.103875

Cohen AS (2003) Paleolimnology: the history and evolution of lake systems. Oxford University Press, New York

Das B, Vinebrooke RD, Sanchez-Azofeifa A, Rivard B, Wolfe AP (2011) Inferring sedimentary chlorophyll concentrations with reflectance spectroscopy: a novel approach to reconstructing historical changes in the trophic status of mountain lakes. Can J Fish Aquat Sci. https://doi.org/10.1139/f05-016

Deshpande BN, Tremblay R, Pienitz R, Vincent WF (2014) Sedimentary pigments as indicators of cyanobacterial dynamics in a hypereutrophic lake. J Paleolimnol 52:171–184. https://doi.org/10.1007/s10933-014-9785-3

Guilizzoni P, Marchetto A, Lami A, Gerli S, Musazzi S (2011) Use of sedimentary pigments to infer past phosphorus concentration in lakes. J Paleolimnol 45:433–445. https://doi.org/10.1007/s10933-010-9421-9

Küpper H, Spiller M, Käpper FC (2000) Photometric method for the quantification of chlorophylls and their derivatives in complex mixtures: fitting with gauss-peak spectra. Anal Biochem 286:247–256. https://doi.org/10.1006/abio.2000.4794

Küpper H, Seibert S, Parameswaran A (2007) Fast, sensitive, and inexpensive alternative to analytical pigment HPLC: quantification of chlorophylls and carotenoids in crude extracts by fitting with gauss peak spectra. Anal Chem 79:7611–7627. https://doi.org/10.1021/ac070236m

Leavitt PR (1993) A review of factors that regulate carotenoid and chlorophyll deposition and fossil pigment abundance. J Paleolimnol 9:109–127

Leavitt PR, Brown SR (1988) Effects of grazing by Daphnia on algal carotenoids: implications for paleolimnology. J Paleolimnol 1:201–213

Leavitt PR, Hodgson DA (2002) Sedimentary pigments. Tracking environmental change using lake sediments. Springer, Dordrecht, pp 295–325

Mikomägi A, Punning JM (2007) Fossil pigments in surface sediments of some Estonian lakes. P EST ACAD SCI 56:239–250

Moss B (1968) Studies on the degradation of Chlorophyll a and carotenoids in freshwaters. New Phyto 67:49–59

Reuss N, Leavitt PR, Hall RI, Bigler C, Hammarlund D (2010) Development and application of sedimentary pigments for assessing effects of climatic and environmental changes on subarctic lakes in northern Sweden. J Paleolimnol 43:149–169, https://doi.org/10.1007/s10933-009-9323-x

Sanchini A, Grosjean M (2020) Quantification of chlorophyll a, chlorophyll b and pheopigments a in lake sediments through deconvolution of bulk UV–VIS absorption spectra. J Paleolimnol 64:243–256. https://doi.org/10.1007/s10933-020-00135-z

Sanger JE, Gorham E (1972) Stratigraphy of fossil pigments as a guide to the postglacial history of Kirchner Marsh, Minnesota. Limnol Oceanogr 17:840–854

Smol JP (1992) Paleolimnology: an important tool for effective ecosystem management. J Aquat Ecosyst Health 1:49–58

Swain E (1985) Measurements and interpretation of sedimentary pigments. Freshwat Biol 15:53–75

Thrane J-E, Kyle M, Striebel M, Haande S, Grung M, Rohrlack T, Andersen T (2015) Spectrophotometric analysis of pigments: a critical assessment of a high-throughput method for analysis of algal pigment mixtures by spectral deconvolution. PLoS ONE 10:e0137645. https://doi.org/10.1371/journal.pone.0137645

Tönno I, Nauts K, Belle S, Nömm M, Freiberg R, Köiv T, Alliksaar T (2019) Holocene shifts in the primary producer community of large, shallow European Lake Peipsi, inferred from sediment pigment analysis. J Paleolimnol. https://doi.org/10.1007/s10933-019-00067-3

Wilson M, Carpenter S (1999) Economic valuation of freshwater ecosystem services in the United States: 1971–1997. Ecol Appl 9:772–783. https://doi.org/10.1890/1051-0761(1999)009[0772:EVOFES]2.0.CO;2

Publisher’s Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.