



Tracking changes in the organic matter in a lake palaeoecosystem: A spectrophotometric approach

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ARTICLE INFO

Available online 15 May 2008

ABSTRACT

The applicability of fluorescence spectrophotometry and absorption spectrophotometry of sediment organic matter dissolved in pore water (pDOM) for detecting changes in homogeneous limnic deposits was examined. Testing was performed on sediment cores collected from a shallow hypertrophic lake, Lake Harku, Estonia, in which prolific algal blooms have occurred for the last 60 years. Although the age-resolved profiles of fluorescence and absorbance characteristics of pDOM exhibit minor temporal changes over the last 100 years, the scatter plots of different pairs of the pDOM optical characteristics reveal several decisive periods that temporally accord well with the stratigraphic changes in subfossil diatoms and green algae, as well as geochemical proxies.

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1. Introduction

Organic matter (OM) has a key role in the functioning of an ecosystem. In an aquatic ecosystem, OM can be produced inside a water body (endogenous OM) or transported from its catchment (exogenous OM). Endogenous OM is characterised by a lower molecular weight and predominantly aliphatic nature, while in exogenous OM components with a higher molecular weight and aromatic structures prevail (McKnight et al., 2001). In many water bodies the main source of OM has altered due to human activity: endogenous OM has become predominant as a result of the enrichment of aquatic systems with mineral nutrients, which favours the thriving of planktonic algae (Smith et al., 1999).

The molecular structure and quantity of OM can be roughly detected from its optical properties. The recording of the spectra is an instrumentally simple and fast technique, which makes the spectrophotometric approach attractive in high-resolution palaeolimnological studies. Earlier applications of fluorescence spectrophotometry

and absorption spectrophotometry on bulk sediments (Wolfe et al., 2002) and on sediment pore water samples (Leeben et al., 2005, 2008; Heinsalu et al., 2007) have proven the capability of these tools in discerning the sources of OM for understanding the dynamics of past environmental changes in lakes. In this study, we tested the applicability of the spectrophotometric approach for detection palaeoenvironmental changes in lacustrine sedimentary OM consisting mainly of endogenous OM (C/N atomic ratio 9.2–10.4; Lepane et al., 2004). Spectra of sediment OM dissolved in pore water (pDOM) were analysed. The following spectral characteristics were considered: (i) fluorescence intensity (emission at a wavelength of ~470 nm by excitation at ~360 nm); (ii) absorbance at 254 nm, both associated with carbon concentration; (iii) their ratio (Stewart and Wetzel, 1980; De Haan and De Boer, 1987); (iv) ratio of the absorbance at 250 and 365 nm (Peuravuori and Pihlaja, 1997); (v) ratio of fluorescence intensity at 470 nm and 520 nm by excitation of samples at 360 nm (McKnight et al., 2001). The values of the ratios are related to the degree of aromaticity of: a high value refers to components with a low degree of aromaticity. In addition to down-core profiles, the changes in pDOM were visualised by constructing scatter plots with different pairs of these spectral

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characteristics. The information obtained from the graphs was compared with the stratigraphy of microfossil remains (diatoms and green algae), temporal changes in pDOM average molecular weight and instrumental monitoring data.

2. Study site, sediment sampling and experimental

Sediment samples were collected from Lake Harku (Estonia), a shallow (mean depth 1.6 m, max depth 2.6 m) small lake (area 1.64 km²) in the temperate zone (59°25' N, 24°37' E). The lake is surrounded by agricultural land and has therefore experienced nutrient enrichment. In 1993–1994 biomanipulation was carried out with the aim of reducing phytoplankton abundance in the lake; however, after a brief improvement for a couple of years, the lake relapsed into the previous state characterised by heavy algal blooms.

A short sediment core was taken in 1992 from the central part of the lake at a water depth of 2.0 m with a plexiglas piston corer. In the laboratory the core was dissected at 1 cm intervals. An additional core was taken at the same location in 2005 using a Willner-type sediment sampler. The cores were correlated on the basis of loss-on-ignition and diatom data. The OM content and carbonate content were determined by loss-on-ignition at 550 °C for 4 h and at 900 °C for 2 h, respectively from each sub-sample. A chronology for the core was established via the vertical distribution of ²¹⁰Pb in the sequence, and the age–depth curve was calculated using the constant rate of supply (CRS) model (Appleby and Oldfield, 1978). The accuracy of the ²¹⁰Pb dating was tested with independent chronological evidence from the down-core distribution of spheroidal fly ash particles (SFAP; Fig. 1), products of fossil fuel burning (e.g. Heinsalu et al., 2007).

Sediment pore water was extracted from the sliced sediments (2005 core) by centrifugation at 2328g for 30 min and clarified by filtration (pore size 0.22 µm); 3D fluorescence spectra of pDOM were obtained over the excitation

spectral range of 240–360 nm and the corresponding emission range of 250–570 nm using a fluorescence spectrophotometer Fluorimager M51 (LDI Ltd.). Absorbance measurements were made with a UV–VIS spectrophotometer Cadas 100 (Dr. Lange). Molecular weights of pDOM were evaluated using a high-performance size exclusion chromatographic method (Lepane et al., 2004). Molecular weights and the polydispersity index were calculated using formulae given by Chin et al. (1998). In selected sediment samples the concentration of pore water dissolved organic carbon (pDOC) was determined. The samples were prepared as recommended in ISO 8245 (1999) and analysed using a DC-80 Total Organic Carbon Analyser (Rosemount–Dohrman).

For the determination of different biological remains the sub-samples were pre-treated according to standard methods: for diatoms according to Battarbee et al. (2001) and for green algae according to Cronberg (1986). The remains of algae were identified and counted under a microscope; a known quantity of external microscopic marker grains was added to the sediment samples to calculate microfossil concentrations and through that annual accumulation rates (ARs) of different taxa. Diatom inferred lake water total phosphorus concentrations (DI-TP) were reconstructed online (<http://craticula.ncl.ac.uk/Eddi/jsp>) using the European Diatom Database combined European TP calibration training set data and the locally-weighted weighted averaging regression (LWWA) model.

3. Results and discussion

Palaeolimnological data (Fig. 2a–e) suggest that over the first half of the 20th century the lake was mesotrophic (DI-TP values 35–60 µg L⁻¹) and, with respect to life form preferences, diatoms were dominated by benthic and epiphytic communities, suggesting clear water conditions. Several lines of palaeolimnological evidence point to increasing influence of human activity on the lake since the 1950s and 1960s. A continuous enhance-

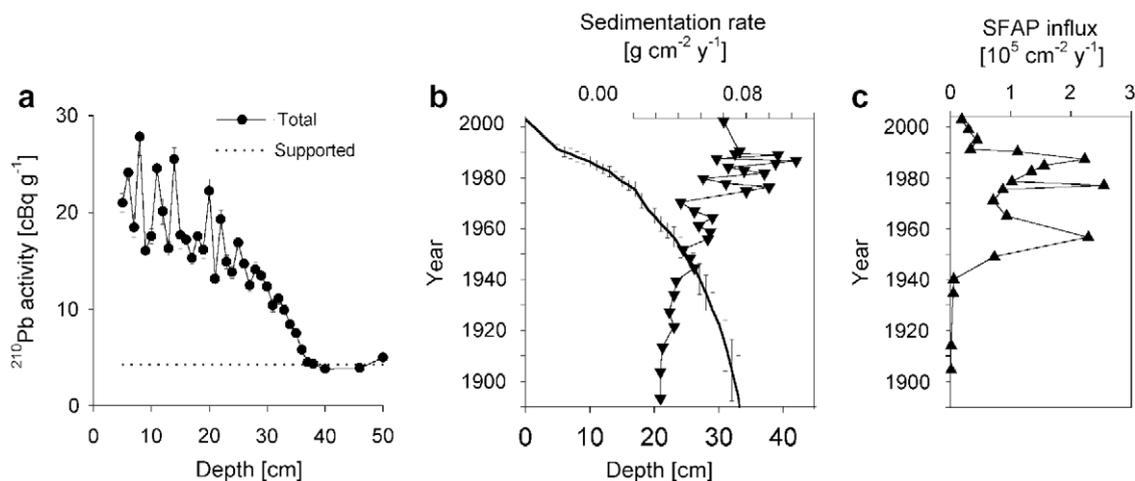


Fig. 1. Dating results for Lake Harku sediment core: (a) ²¹⁰Pb activity, (b) ²¹⁰Pb sediment age and sedimentation rate calculated with the CRS model, (c) sediment accumulation curve of spheroidal fly ash particles (SFAP) in ²¹⁰Pb age scale.

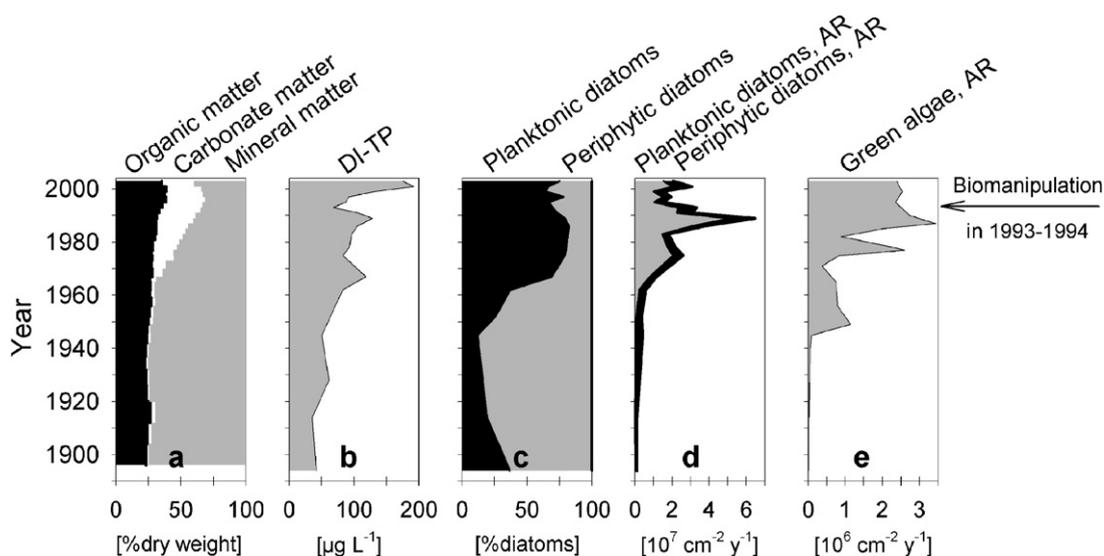


Fig. 2. Age-related changes in (a) sediment composition, (b) diatom inferred lake water total phosphorus concentration (DI-TP) and (c–e) microfossil assemblages in sediment records from Lake Harku. AR = annual accumulation rate.

ment in AR of planktonic diatoms and green algae suggests expansion of phytoplankton productivity. This floristic change coincides with a substantial rise in DI-TP, indicating high nutrient concentrations. In addition, the composition of the sediments suggests that, due to its higher rate of photosynthesis, phytoplankton consumed lake-water CO_2 , causing an alkaline shift in the pH and promoting precipitation of carbonate. Moreover, results from sediment proxies coincide with limnological data for Lake Harku since the 1970s, which report massive algal blooms (phytoplankton biomass 100 mg L^{-1}) and very low (20–30 cm) water transparency values (e.g. Lepane et al., 2004). A short-term improvement in the lake ecosystem as a result of biomanipulation activity in the mid-1990s can be seen in the sediment proxy data; however, the lake quickly returned to the previous state characterised by nuisance algal blooms.

The profiles of the pDOC concentration, fluorescence intensity and absorbance of pDOM (Fig. 3a–c) exhibit an opposite pattern compared to the geochemical and microfossil profiles – the values slowly decrease with the prevalence of planktonic algae, with the lowest values in the 1970s and 1980s, and sharply increase in the 1990s when temporarily the water column production somewhat declined after biomanipulation. The observed decline in the 1970s and 1980s can be explained by the capability of mineral substances to adsorb pDOM (Thimsen and Keil, 1998). The temporal distribution of average molecular weight of pDOM (Fig. 3g) and of the polydispersity index (Fig. 3h), which is a quantitative measure of the molecular weight distribution of OM in a mixture, shows no obvious trend of increase or decrease, suggesting that, over the 20th century, the sources of OM in the lake and processes responsible for its transformation have remained unchanged. Spectral

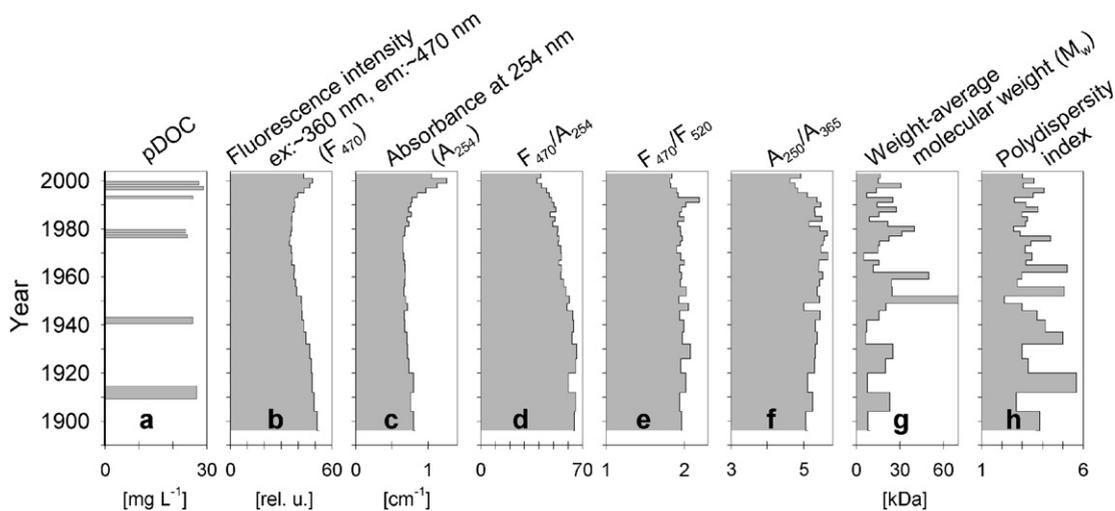


Fig. 3. Age-resolved profiles of (a) the concentration of sediment pore water dissolved organic carbon (pDOC) and (b–f) optical and (g,h) molecular characteristics of pore water dissolved organic matter (pDOM).

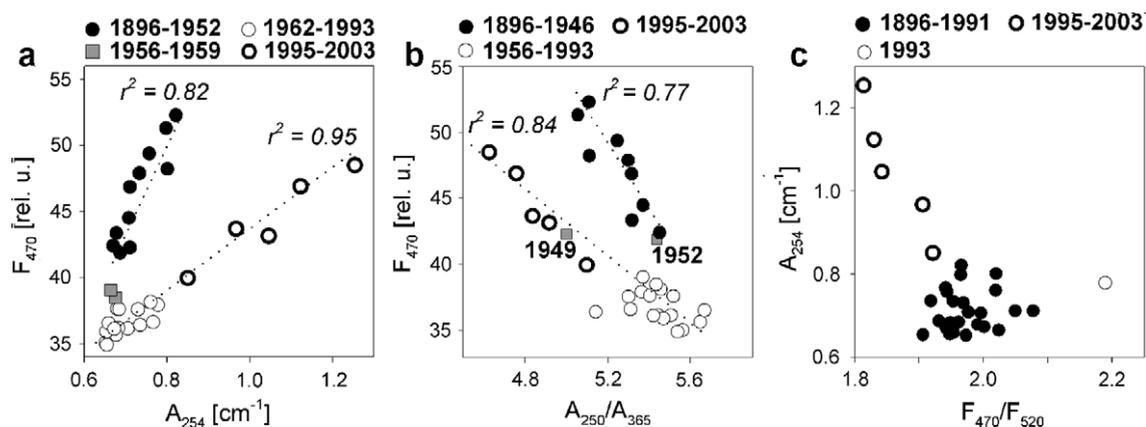


Fig. 4. Scatter plots of different quantitative and qualitative measures of pore water dissolved organic matter resolved from its fluorescence and absorption spectra. Numbers in bold indicate years; correlation coefficients between the measures for the referred period are in italic. Transition years between the periods are indicated by grey squares.

characteristics related to the molecular size and weight structure of pDOM also demonstrate only very slight changes in their temporal distribution (Fig. 3d–f). In spite of the relatively monotonous behaviour of these optical characteristics of pDOM in the sediment record, their scatter plots (Fig. 4a–c) clearly demonstrate that the type of accumulated OM has changed. Fig. 4a and b shows that a transition in the type of accumulated OM took place from the late 1940s to the late 1950s, which coincides well with the onset of the domination of planktonic algal species. According to Fig. 4c, some changes in the type of accumulated OM also occurred in the 1990s; this is a decade when, due to biomanipulation, the conditions in the lake improved for a while. The high values of fluorescence ratio (1.8–2.2; Fig. 4c) through the whole 20th century imply that the sediment pDOM of Lake Harku is mainly derived from algae (McKnight et al., 2001). Therefore, the changes in the character of pDOM in the upper sediment layers are not caused by alteration in its source, but may be a result of changes in biogeochemical processes due to intensification of algal blooms.

The study demonstrated that fluorescence spectrophotometry and absorption spectrophotometry of pDOM can be helpful tools for tracking qualitative changes in sedimentary OM.

Acknowledgements

The research was supported by the Estonian Science Foundation (Grant Nos. 5582, 6720, 6995). We thank T. Laur (Tallinn Water Ltd.) for his technical help, J. Klõšeiko (Estonian University of Life Sciences) for software support and V. Arikese (Estonian Maritime Administration) for valuable discussions on optical measurements. Helpful comments and suggestions provided by H.R. Harvey and an anonymous referee are acknowledged.

Associate Editor—H.R. Harvey

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