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## Spring temperature variability and eutrophication history inferred from sedimentary pigments in the varved sediments of Lake Żabińskie, north-eastern Poland, AD 1907–2008



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#### ABSTRACT

Varved lake sediments are excellent natural archives providing quantitative insights into climatic and environmental changes at very high resolution and chronological accuracy. However, due to the multitude of responses within lake ecosystems it is often difficult to understand how climate variability interacts with other environmental pressures such as eutrophication, and to attribute observed changes to specific causes. This is particularly challenging during the past 100 years when multiple strong trends are superposed.

Here we present a high-resolution multi-proxy record of sedimentary pigments and other biogeochemical data from the varved sediments of Lake Żabińskie (Masurian Lake District, north-eastern Poland, 54°N–22°E, 120 m a.s.l.) spanning AD 1907 to 2008. Lake Żabińskie exhibits biogeochemical varves with highly organic late summer and winter layers separated by white layers of endogenous calcite precipitated in early summer. The aim of our study is to investigate whether climate-driven changes and anthropogenic changes can be sepa-

rated in a multi-proxy sediment data set, and to explore which sediment proxies are potentially suitable for long quantitative climate reconstructions. We also test if convoluted analytical techniques (e.g. HPLC) can be substituted by rapid scanning techniques (visible reflectance spectroscopy VIS-RS; 380–730 nm).

We used principal component analysis and cluster analysis to show that the recent eutrophication of Lake Zabińskie can be discriminated from climate-driven changes for the period AD 1907–2008. The eutrophication signal (PC1 = 46.4%; TOC, TN, TS, Phe-*b*, high TC/CD ratios total carotenoids/chlorophyll-*a* derivatives) is mainly expressed as increasing aquatic primary production, increasing hypolimnetic anoxia and a change in the algal community from green algae to blue-green algae. The proxies diagnostic for eutrophication show a smooth positive trend between 1907 and ca 1980 followed by a very rapid increase from ca. 1980  $\pm$  2 onwards. We demonstrate that PC2 (24.4%, Chl-*a*-related pigments) is not affected by the eutrophication signal, but instead is sensitive to spring (MAM) temperature (r = 0.63, p<sub>corr</sub> < 0.05, RMSEP = 0.56 °C; 5-yr filtered). Limnological monitoring data (2011–2013) support this finding.

We also demonstrate that scanning visible reflectance spectroscopy (VIS-RS) data can be calibrated to HPLC-measured chloropigment data and be used to infer concentrations of sedimentary Chl-a derivatives {pheophytin a + pyropheophytin a}. This offers the possibility for very high-resolution (multi)millennial-long paleoenvironmental reconstructions.

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#### 1. Introduction

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simon.lobsiger@gmx.ch (S. Lobsiger), daniela.fischer@giub.unibe.ch (D. Fischer), geowt@univ.gda.pl (W. Tylmann), a.bonk@ug.edu.pl (A. Bonk), filipiak@univ.gda.pl (J. Filipiak), martin.grosjean@oeschger.unibe.ch (M. Grosjean). High-resolution quantitative climate reconstructions across the world are required to place recent changes from local to planetary scales into a long-term perspective, to evaluate the causes (detection and attribution) and to anticipate the challenges of future climate change (Masson-Delmotte et al., 2013; PAGES 2 k Consortium, 2013).

Lake sediments are valuable natural archives recording physical, chemical and biological changes of natural and anthropogenic origin in

the recent and more distant history of the Earth. Varved lake sediments, in particular, hold great potential due to their annual resolution and high chronological precision and accuracy (Zolitschka, 2007). Varved lake sediments have been successfully investigated using a wide range of sedimentological, bio-geochemical and biological proxies to assess environmental (trophic state, land use, acidification, pollution) and climatic changes (O'Sullivan, 1983; Pienitz and Lotter, 2009; Ojala et al., 2012).

Due to the multitude of impacts and responses within lake ecosystems, one of the key issues is to understand how climate variability interacts with other environmental pressures such as eutrophication or land use changes (Kienel et al., 2005, 2013). This is particularly challenging during the 20th and early-21st centuries when strong simultaneous covariant trends in the atmosphere–catchment–lake system (climate, land use, nutrient cycles, and aquatic food web) are superposed. Thus discriminating climatic from anthropogenic effects is relevant with regard to climate research (Adrian et al., 2009) as well as ecosystem management (Smith et al., 2006; Hobæk et al., 2012).

Sedimentary pigments provide valuable information about environmental and climate changes. In general, changes in the pigment composition and stratigraphy reflect variations in the phytoplankton structure and abundance (Leavitt and Hodgson, 2001), which in turn reflects changes in light availability, temperature, nutrients, lake stratification, food web and some other factors (Wetzel, 2001). Several studies across the world have demonstrated that sedimentary pigments can be used to infer past climate changes in Scandinavia and Central Europe (Lami et al., 2000), Antarctica (Hodgson et al., 2005; Chen et al., 2013), Mongolia (Nara et al., 2005), Chile (von Gunten et al., 2009a) and Nepal (Lami et al., 2010) or to document changes in the trophic levels of lakes in Florida (Waters et al., 2005), Chile (von Gunten et al., 2009b), Sweden (Reuss et al., 2010), Hungary (Korponai et al., 2011) and Estonia (Leeben et al., 2013) among others.

Since pigment measurements are quite convoluted and expensive (Reuss et al., 2010), long and high-resolution reconstructions are difficult to obtain. Recent advances in reflectance spectroscopic techniques in the visible-near-infrared range of 400–1000 nm (VIS-RS) have shown that, although the pigment measurements are less specific, reflectance spectra can be used to approximate sedimentary chlorophyll *a*, Chl-*a* derivatives (chlorins) and carotenoids (Rein and Sirocko, 2002; Das et al., 2005; Wolfe et al., 2006; Michelutti et al., 2010; Chen et al., 2013). In specific cases, changes in the stratigraphy and abundance of these pigments may reflect climate variability (Rein et al., 2005; von Gunten et al., 2009a; Saunders et al., 2013). Scanning VIS-RS techniques, in particular, hold great potential for high-resolution environmental reconstructions, but these methods are still in their infancy.

A recent comprehensive survey by Tylmann et al. (2013a) in northeastern Poland, uncovered the presence of several postglacial lakes that contain undisturbed continuous sequences of annually laminated sediments with biochemical varves. These varves provide highly precise and accurate chronologies (Kinder et al., 2013; Tylmann et al., 2013b). These lakes show mostly anoxic conditions in the hypolimnion and the sediments are highly organic and anoxic thus providing best conditions for the preservation of sedimentary pigments (Leavitt, 1993; Reuss et al., 2005). Moreover, Poland is a very interesting area because, situated in the centre of Europe, its climate reflects approximately average European conditions (Luterbacher et al., 2010). Therefore, the varved lake sediments in NE Poland provide unique opportunities for paleoclimate research.

Here we present a multi-proxy data set with sedimentary pigments and other biogeochemical data from the varved sediments of eutrophic Lake Żabińskie (Masurian Lake District) for the recent past (1907– 2008 AD). The aims of our study are (i) to investigate which proxies are diagnostic to differentiate climate-driven changes from changes induced by eutrophication and anthropogenic activities and (ii) to explore whether rapid reflectance spectroscopic techniques are able to approximate expensive but specific pigment measurements (HPLC). In more general terms, both aims target the question whether the sediments of Lake Żabińskie are a suitable archive for millennial-long quantitative high-resolution paleoclimatic reconstructions. Which are the best proxies for that purpose, and which are the most suitable techniques to acquire the data? We will show that, in this particular lake, (i) Chl-*a* derivatives (pheophytin *a* and pyropheophytin *a*) can be used to reconstruct spring (March–May) temperatures and (ii) scanning visible reflectance spectroscopy (VIS-RS) data can be calibrated to HPLC data and be used to infer concentrations of Chl-*a* derivatives in these lake sediments.

#### 2. Study site

Lake Żabińskie (54°07′54″ N; 21°59′01″ E; 120 m a.s.l.) is a postglacial lake located in the Masurian Lake District, north-eastern Poland (Fig. 1a). The lake has formed after the deglaciation of the Fennoscandian Ice Field around 15 kyr BP (Kaufmann et al., 2000). The geology of the area consists mainly of Quaternary glacial and fluvio-glacial deposits composed of morainic till as well as fluvio-glacial and fluvial sands and gravels (Szumański, 2000).

The climate of the Masurian Lake District belongs to the humid continental warm summer type (Dwb) according to the Köppen classification. Monthly mean temperatures downscaled for Lake Żabińskie range from -3 °C in January to 18 °C in July (Fig. 1b). The total annual precipitation is 610 mm. Snow accounts for approximately two thirds of winter precipitation (December–March). Correlation field analysis of spring March–May MAM temperature (the target of our study; CRU TS 3.0 data; Mitchell and Jones, 2005) shows that the study site is a good predictor (r > 0.7, p < 0.001) for spring temperature in most areas of Western, Central and Eastern Europe, and southern Scandinavia (Fig. 1b).

The catchment of the lake has experienced important human impacts during the 20th century with the construction of buildings between AD 1910 and 1920 at the northern lake shore directly (Fig. 1a). A holiday resort was also established between AD 1950 and AD 1960 and enlarged in the 1970s and mid-1980s. The resort centre is today privately owned and connected to the sewage treatment system only since AD 1998. The use of artificial fertilizers for agriculture increased considerably in this region after AD 1965–1975.

Lake Żabińskie is an exorheic lake. It receives water from the forested north-eastern part of its catchment mainly (Lake Purwin; Fig. 1a) and from two southern streams supplying water from cultivated fields. The lake discharges westward into the larger Lake Gołdopiwo. The lake is dimictic (spring and fall overturn usually complete except in warm winters like 2012/2013) and experiences summer stratification between May and October (Fig. 2). The thermocline is at around 5–10 m and anoxic conditions establish in the hypolimnion during summer. The water surface is covered by ice during winter months (generally January to early March).

Today, Lake Żabińskie is eutrophic. Distinct algal blooms are observed during the growing season and are typically associated with very low water transparency (Secchi disk visibility < 1.2 m). Chl-*a* concentrations in the epilimnion are high in spring and early summer following the ice break-up with a maximum in May (158  $\mu$ g·L<sup>-1</sup> in 2012, 84.2  $\mu$ g·L<sup>-1</sup> in 2013; Fig. 2). According to Kufel (2001), light becomes limiting in early summer and blue-green algal blooms develop during the rest of the summer season, which is typical for Masurian lakes. The electric conductivity through the water column varies in the range of 350–450  $\mu$ S·cm<sup>-1</sup> and pH fluctuates between 6.9 and 9.4.

Lake Żabińskie forms biogeochemical varves with a spring-to-fall layer composed of endogenous calcite grains, diatoms and chrysophytes and a winter layer rich in amorphous organic matter (Tylmann et al., 2013a).

#### 3. Material and methods

#### 3.1. Sediment coring and sampling

A 51-cm long sediment core was retrieved at the deepest point of Lake Żabińskie (Fig. 1b) using a gravity corer (UWITEC,  $\Phi$  6 cm) in

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