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Sedimentary Bacteriopheophytin *a* as an indicator of meromixis in varved lake sediments of Lake Jaczno, north-east Poland, CE 1891–2010

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ABSTRACT

Trends in eutrophication and meromixis pose serious threats to water quality and biodiversity in freshwater ecosystems around the world. Because long-term observational data rarely exist, it is very difficult to assess whether meromixis is the result of anthropogenic impacts, climate variability, natural ecosystem development or a combination of these factors. Lake sediment proxy-data may help understand how and why eutrophication and meromixis occurred and disappeared in the past. In this study, we present a novel method and proxy to investigate past episodes of meromixis and hypolimnetic anoxia recorded in lake sediments. We use high-resolution (70×70 μm/pixel) calibrated hyperspectral imaging of a varved lake sediment core from meromictic Lake Jaczno (north-east Poland), to quantitatively map the spatial distribution of Bacteriopheophytin *a* (Bphe *a*) at very high sub-varve (i.e. seasonal) resolution. Bphe *a* is a bacterial pigment and stable degradation product of Bacteriochlorophyll *a* (Bchl *a*), which is produced by anoxygenic phototrophic bacteria (APBs) at the chemocline of meromictic lakes. Using sedimentary Bphe *a* we infer episodes of meromixis (i.e. long-term hypolimnetic anoxia) and changing mixing conditions (i.e. seasonal temperature, event-based water mixing) for the past ca. 120 years. Absence of meromixis occurred on several occasions. From the beginning of our record in CE 1891 until ca. CE 1918, meromixis was not observed. During this time, green pigments (mainly chlorophyll *a* [Chl *a*] and diagenetic products) produced by phototrophic algae were deposited while Bphe *a* was absent. This suggests that regular lake overturning prevented the formation of a persistent chemocline. Bphe *a* was identified before CE 1890 (Butz et al. 2015), but over the studied period 1891–2011, meromixis was established in CE 1918 and generally persisted through modern times. However, short-term interruptions of the chemocline were observed following events of rapid sedimentation (CE 1943, CE 1946, CE 1950) and after a strong pulse of terrigenous material in CE 1978. These events were able to break up meromixis for a short period. After a few years, the system always turned back to meromixis. After ca. CE 1960, meromixis became particularly persistent. This can be attributed to the increased use of fertilizers (causing eutrophication) and warm summers after CE 1990. While interannual summer temperature variability played a major role in the mixing regime until ca. CE 1920, the climatic influence generally decreased in the following decades as the lake remained persistently in a meromictic state due to eutrophication. However, the climatic fingerprint remained detectable for very warm or cold summers.

1. Introduction

Eutrophication of lakes and oceans has increased globally and developed into a serious environmental threat (Smith et al., 1999; Diaz, 2001; Smith, 2003; Diaz and Rosenberg, 2008; Jenny et al., 2016). In their planetary boundary framework, Steffen et al. (2015) identified nitrogen and phosphorus cycles as potential high risk factors to environmental boundaries that can support contemporary human societies safely. Because of eutrophication, many lakes increasingly undergo depletion in hypolimnetic oxygen, either seasonally or for longer periods. This may result in negative impacts such as blooms of toxic algae, remobilization of redox-sensitive metals or in the development of bacterial communities. Thus, water may degrade substantially in quality and even become toxic (Quinlan and Smol, 2001; Friedrich et al., 2014).

Eutrophication can occur slowly due to natural changes or much faster due to anthropogenic causes (Sawyer, 1966). Often, intensified

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land-use and application of fertilizers and animal manure lead to eutrophication of lakes (Correll, 1998; Carpenter, 2005; Elser et al., 2007).

Excess nutrients in combination with warm temperatures lead to an increase in the primary productivity of a lake. Hence, deposition and decomposition of organic matter increases, which often leads to a depletion of oxygen in deep waters (Jenny et al., 2013). Warmer temperatures also result in longer and stronger temperature stratification during the summer months (Adrian et al., 1995; Livingstone, 2003; Foley et al., 2012). In lakes with incomplete mixis, anoxia in the hypolimnion may become permanent. In such environments, reducing conditions prevail and remobilization of chemical species from the sediments may occur, which increases the specific density in the hypolimnion and a chemocline may develop (Davison, 1993). This process is often driven by thresholds (e.g. redox, pH), enforced by positive feedbacks (redox cycle) and may be persistent for prolonged periods (meromixis).

Unfortunately, long-term environmental data series on oxygen depletion in lakes rarely exist. This makes it difficult to assess the causes and dynamics of hypolimnetic anoxia and the stability of the chemocline. Potentially, lake sediments may provide this information. Today, however, only few sediment indicators exist to infer past lake water anoxia. Some species of chironomids have adapted to low or depleted oxygen environments and can indicate anoxic conditions (Brodersen and Quinlan, 2006). Other studies use the different redox behaviour of Mn and Fe (Wersin et al., 1991; Loizeau et al., 2001; Naeher et al., 2013). The reduction of Mn occurs faster than that of Fe under anoxic conditions and, therefore, remobilization occurs more easily from the sediment while Fe accumulates. This leads to lower Mn/Fe ratios in the sediments. In contrast, high Mn/Fe ratios occur only under oxic conditions because Fe oxidizes faster than Mn (Naeher et al., 2013). However, a potential problem with this method is that increased Fe inputs to sediments may originate from terrestrial sources and have little to do with redox conditions in the lake. Moreover, the method was used mainly in lakes with seasonal anoxia rather than constant anoxia (Naeher et al., 2013). In environments of constant anoxia Mn and/or Fe may remain dissolved in the lake water (Davison, 1993).

Anoxygenic phototrophic bacteria (APB) may be very good indicators for long-term anoxia (Schmidt et al., 2002; Rogozin et al., 2011; Rogozin et al., 2012). Although APBs are very versatile organisms and can occupy very different habitats (Van Gemerden and Mas, 1995), the preferred habitat of planktonic APB species is the transition zone between oxic and anoxic conditions (chemocline) in constantly stratified (i.e. meromictic) lakes, where reduced sulphur compounds are abundant and oxygen levels are low. Limiting factors for bacterial blooms are, aside from nutrients and sulphides, the stability of and light availability at the chemocline. Therefore, APBs respond most sensitively to changes in light intensity (Parkin and Brock, 1980) and vertical lake mixing (Van Gemerden and Mas, 1995).

While APBs in the water column of lakes are well studied (e.g. Montesinos et al., 1983; Guerrero et al., 1985; Overmann et al., 1991; Lunina et al., 2013), only few studies deal with biomarkers of APBs in sediments (Züllig, 1986; Hodgson et al., 1998; Dreßler et al., 2007). Some APBs produce Bacteriochlorophyll *a* (Bchl *a*), a diagnostic pigment for photosynthesis. Although Bchl *a* is highly unstable, it may be preserved in sediments in the form of its stable degradation product Bacteriopheophytin *a* (Bphe *a*). Some APBs can also live under aerobic conditions; however, oxic conditions mostly inhibit the production of Bchls (Cohen-Bazire et al., 1957; Hurlbert, 1967; Blankenship, 2013). Hence, the presence of Bphe *a* in the sediment may be indicative of prolonged anoxic conditions and thus help diagnose long-term lake stratification and the presence of a chemocline (i.e. meromixis).

Measurement of sedimentary pigments, however, is complex and expensive (Reuss et al., 2005). Recently, novel spectral reflectance-based analytical tools were developed and open new ways in the analysis of sedimentary pigments. These scanning methods offer unprecedented insight into pigment distributions at very high sampling resolutions (μm-scale; i.e. sub-varve or seasonal resolution) and at a low cost (Grosjean et al., 2014; Butz et al., 2015). In particular, chlorophyll-type pigments and carotenoids have been successfully calibrated to reflectance spectra (Rein and Sirocko, 2002; Das et al., 2005; Rein et al., 2005; Wolfe et al., 2006; Amann et al., 2014). Also Bchl *a* and its degradation products are well characterized by spectral absorption in the near infrared range between 800 and 900 nm (Scheer, 2006; Ji et al., 2009; Blankenship, 2013). As a proof of concept, Butz et al. (2015) recently demonstrated that hyperspectral imaging (HSI) data can be calibrated to sedimentary Bphe *a* concentrations ($R^2_{HPLC;HSI} = 0.89$, RMSEP = ~10%), which opens new possibilities for the study of lake sediments.

Here, we apply the Bphe *a* calibration model developed by Butz et al. (2015) to HSI data for Lake Jaczno (north-east Poland) and present a seasonally resolved reconstruction of meromixis since CE 1891. Meromixis is inferred from the distribution and quantity of sedimentary Bphe *a*. The goals of our study are: (i) to test whether HSI-inferred Bphe *a* concentrations can be used to reconstruct meromixis in a lake; (ii) to investigate how meromixis developed and disappeared; and (iii) whether these changes can be related to climatic, anthropogenic or internal lake processes.

2. Site description

Lake Jaczno (163 m a.s.l.) is located in the Suwałki Lake District in north-east Poland (54°16′26.3″N; 22°52′20.3″E, Fig. 1A). The region is characterized by post-glacial deposits, glacial tills, sand, gravel, boulders and silts, which were deposited after the deglaciation of the Fennoscandian ice field ~15,000 BP at the end of the Weichselian glaciation (Kaufmann et al., 2000). Thus, most of the lakes in this area have formed in dead ice holes. Lake Jaczno has five distinct basins interconnected by shallow sills (Fig. 1B). The total surface area amounts to ~0.41 km^2. Exchange of water between the basins is limited. The catchment of the lake spans an area of ~9 km^2 (Fig. 1C). Most of the catchment (~8 km^2) drains into the northern basin. The catchment of the basin with the coring site consists mostly of forests and small areas of arable land. Lake Jaczno is exorheic with a small outflow draining the southernmost basin. The bathymetric map shows substantial differences in the depths of the basins. The coring site is close to the deepest point in the lake (25.7 m, Fig. 1B). Lake Jaczno is currently mesotrophic (Zieliński et al., 2006; Tylmann et al., 2013).

The climate in the region is continental with a mean annual temperature of ~6.4 °C and mean annual precipitation of ~600 mm (Suwalki meteorological station). Lakes are commonly ice-covered during the winter months between December and March (Amann et al., 2014).

Limnological parameters from CE 2013 indicate meromictic conditions with chemical and temperature stratification of the water column (Fig. 1D). Chemical stratification persisted for the whole year. The oxygen profiles showed that the hypolimnion was anoxic during the entire year. Electrical conductivity generally increased with depth while pH (pH: 7.5–8.5) decreased. Both parameters showed a chemocline at ~7–11 m with a mixolimnion from 0 to 7 m and a monimolimnion from 11 to 25.7 m. The profile of green pigments (fluorescence at 685 ± 15 nm, which is mostly due to Chl *a* and diagenetic products but also Bchl *e* in small quantities (Causgrove et al., 1992)) shows a complex seasonal pattern. In March, low concentrations of pigments were found in the top 3 m. A high peak of pigment concentration followed during May and June at a depth of 3–7 m. In August, two distinct peaks were observed at a depth of ~9 m and ~11 m. In October, the peak at ~11 m prevailed while the peak in the epilimnion disappeared.

3. Methods

A 260 cm long sediment core was collected using a UWITEC gravity corer (9 cm diameter) in September 2011. In a second field campaign (2013) temperature, conductivity, oxygenation, pH and green pigments